

PRINCIPLES OF STEELMAKING

DR.-ING. A. K. BISWAS



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To

**Professor DR.—ING., DR.—ING. Eh.
HERMANN SCHENCK**

PREFACE

The art of steelmaking has changed to a science in the last three decades. This has primarily been possible due to the systematic application of the data, obtained from equilibrium experiments concerning steelmaking reactions. There is scarcely any doubt that theory still lags behind the practice as far as steelmaking is concerned. But, since every metallurgical operation consists of a series of simultaneous or progressive physical or chemical reactions, the study of physico-chemical principles of steelmaking has gone a long way to help the practical steelmaker whose primary object is to alter the works practice according to the effectiveness of the reactions. This has led not only to higher efficiency, economy and quality but also to developing newer, better and cheaper methods of production.

Several earlier workers have tried to explain various steelmaking phenomenon with the help of laboratory data. Amongst them, R. Durrer and H. Schenok have been pioneers in systematically recording and co-ordinating the theory vis-a-vis practice in their famous books. With the same end in view and with almost the same method of representation I have written this book, presenting more recent data of various research investigations and relating them to practice as far as possible.

Steelmaking mostly consists of interactions between various components and phases. The equilibrium systems given in Chapter III will help in the understanding of the basic physico-chemical principles involved in the reactions of carbon, silicon, manganese, chromium, phosphorus, sulphur and others described in the subsequent chapters. Those who wish to review the steel-making practice will find a brief discussion in Chapter II which will help understanding the chapters that follow.

As most of the recent steelmaking data are unfortunately dispersed in the transactions and proceedings of numerous learned societies, it is difficult for the steel-makers, teachers and students alike to locate the required information as quickly as one would like. It is hoped this book will enable to overcome these difficulties and prove a useful reference book for teachers and steelmakers

and at the same time a convenient text-book for the student of ferrous production metallurgy.

I wish to record my indebtedness to various publishers and learned societies who have kindly given permission to reproduce the illustrations as well as to various authorities quoted in the references.

I am specially indebted to Professor Hermann Schenck for his kind permission to draw materials freely from his extensive work and this book is dedicated to him for his great contributions to the science of steelmaking.

I record here my deepest gratitude to my wife Nilima for her untiring support and to Messrs. R. K. Chowla, P. K. Sen Gupta, Ajoy Biswas and P. Ekka for their help and encouragement.

Finally, I thank the publishers for their help and wholehearted cooperation.

Burnpur, West Bengal.
November, 1963

A. K. BISWAS

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PRINCIPLES OF STEELMAKING

CHAPTER I

INTRODUCTORY PHYSICAL CHEMISTRY

IRON exists in nature mainly as its oxides and is obtained by their reduction. During reduction, impurities like carbon, silicon, manganese, phosphorus, sulphur and others enter the so-called pig-iron. Steel is produced from the pig by the removal of these impurities mainly as their oxides in the form of slag. Since iron, steel, slag are all obtained in liquid state, their metallurgy is essentially a high temperature chemistry. A theoretical treatment of steelmaking principles is rendered difficult by the presence of solid, liquid and gas phases (refractory lining, molten slag and metal, air, oxygen, combustion gases) on the one hand and numerous components in the systems on the other. Further complication arises because of the doubt whether the interactions amongst the various components and phases reach equilibrium at all. Even with all these difficulties, it is possible to obtain a rough estimate of the extent of reactions from the study of the physico-chemical principles and the thermodynamical and kinetic data.

The physico-chemical principles of metallurgical processes have been discussed elsewhere by the author.¹ The essentials are given in this chapter so as to enable a better understanding of the treatment in the text that follows.

Gas law

By the combination of the well-known Boyle's and Charle's laws, any gaseous system can be completely defined by certain physical conditions—temperature, pressure and volume—and the relationship of these values can be expressed in the condensed equation :

$$PV = nRT \quad 1.1$$

where P = pressure

V = volume

n = number of gas moles.

T = absolute temperature.

R = a constant commonly termed as gas constant

= 0.08203 litre atmosphere/deg/mole

= 2 cal/deg/mole

= 8.314 j/deg/mole

The heat absorbed by a substance divided by the increase in temperature is known as the *heat capacity* of the substance. At constant pressure,

$$C_p = dH/dT \quad 1.7$$

When 1 mole of the substance is involved it is called *molar heat capacity*; for 1 gm, it is specific heat.

These are not constant quantities. Generally, they decrease with increase of temperature. They are usually given in thermal data in the form,

$$C_p = \alpha + \beta T + \gamma T^{-2} \quad 1.8$$

(α, β, γ , being constants evaluated from experiments).

The change in enthalpy between two temperatures can be obtained by combining Eqs. 1.7 and 1.8 and integrating :

$$\Delta H = H_2 - H_1 = \left[\alpha T + \frac{1}{2} \beta T^2 - \gamma T^{-1} \right]_{T_1}^{T_2} \quad 1.9$$

For the sake of convenience and uniformity H_1 for all substances are given at 298°K which enables the determination of the relative value of H_2 at any other temperature.

Effect of temperature upon heat of reaction

The effect of temperature in a chemical reaction involves both enthalpies and heat capacities. Their changes are depicted as :

$$\Sigma C_p(\text{products}) - \Sigma C_p(\text{reactants}) = \Delta C_p$$

$$\Sigma H(\text{products}) - \Sigma H(\text{reactants}) = \Delta H$$

The value of ΔC_p is obtained by subtracting the sum of the heat capacities of reactants from that of the products. ΔH is calculated similarly, the enthalpies of elements at 298°K being taken as zero. For the change of enthalpy

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT \quad 1.10$$

If between the temperature ranges 298 to T a substance undergoes phase transformations, viz. fusion or evaporation, then

$$H_T = \int_{298}^{T_{m.p.}} C_p(s) \cdot dT \pm H_f + \int_{T_{m.p.}}^{T_{b.p.}} C_p(l) \cdot dT \pm H_e + \int_{T_{b.p.}}^T C_p(g) \cdot dT \quad 1.11$$

Equilibrium constant. Activity

The equilibrium in any reacting system is reached when the forward reaction of the reactants and the reverse reaction of the products assume the same velocity.

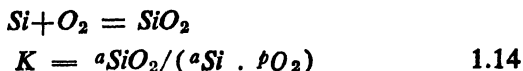
Since according to the law of mass action (LMA), the rate of any chemical reaction is proportional to the active mass or molecular concentration of the reactants, it can be deduced that for the general reaction



$$\text{at equilibrium, } K_c = \frac{[C]^q \cdot [D]^r}{[A]^n \cdot [B]^m} \quad 1.13$$

where the alphabets inside the brackets denote the molar concentrations and K_c , the equilibrium constant in terms of concentration. This constant is a function of temperature.

The LMA in terms of actual concentrations is, however, obeyed only in ideal cases where there exists no mutual attractions or repulsions amongst the atoms and the molecules in the reacting system. In a non-ideal system, the apparent concentrations or 'activity' terms are used. In case of a gas, its partial pressure is substituted. As for example, for the reaction



The actual concentration of any substance in solution is depicted as *mol fraction* which is defined as the ratio of the number of its moles to the total number of moles of all the substances present in the solution and is denoted by N . The number of moles can be simply calculated by dividing the weight per-

centage of each constituent with the respective atomic or molecular weight. In an ideal solution this mol fraction is equal to 'activity' and a plot of a and N gives a straight line known as *Raoult's line* (Fig. 1.1). In a non-ideal solution of, say, A and B , the activity of B is no longer equal to its mol fraction and we write

$$a_B = f_B \cdot N_B \quad 1.15$$

where f_B is a factor called *activity coefficient*. It is a factor by which the extent of departure from Raoult's law is measured. Evidently, the activity of a pure substance is unity, in which case $f_B = 1$.

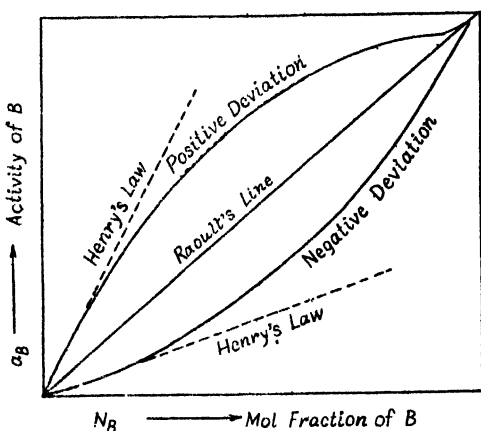


Fig. 1.1—Schematic diagram of Raoult's and Henry's lines showing the positive and negative deviations from the former.

Generally, most of the solutions show deviations from the Raoult's law, which may be positive or negative as shown in Fig. 1.1. A positive deviation occurs when the attraction between A and B is less than that between A and A or between B and B , whereby

$$a_B > N_B \text{ or } a_B/N_B > 1 \text{ or } f_B > 1 \quad 1.16$$

When the attraction between A and B is greater than that between A and A or B and B , there occurs a negative deviation,

$$\text{whereby } a_B/N_B < 1 \text{ or } f_B < 1 \quad 1.17$$

When the attraction between A and B is the same as between A and A or B and B , the solution is ideal, i.e.

$$a_B = N_B \text{ and } f_B = 1$$

In phase diagrams, the positive deviation is shown where the cooling curve is rather flat indicating a tendency for separation (cf. Figs. 3.23 and 3.39) or where a 'miscibility gap' is present (cf. Fig. 3.25). A negative deviation is indicated by compound formation, heat evolution, etc.

Henry's Law

From Fig. 1.1., in a non-ideal solution of great dilution, i.e. where N_B is very small, the curve follows more or less a straight line as can be seen from the dotted lines. In this range of dilution where B acts as a solute rather than a solvent, the activity is proportional to the mol fraction though they are not equal. It illustrates the so-called Henry's line which deals with the solutes.

It is possible to define a standard state for the Henry's law, i.e. the activity of a solute is unity in an infinitely dilute solution (1% solution). In such a case, the activity terms in the equilibrium constant equation can be replaced by wt.%. This has importance in steelmaking because the amounts of impurities present there are small. As for example, in the reaction



$$K' = a_{\text{SiO}_2} / (a_{[\text{Si}]} \cdot a^2_{[\text{O}]})$$

$$\text{or} \quad K = a_{\text{SiO}_2} / (\%[\text{Si}] \cdot \%[\text{O}]^2)$$

In cases where even Henry's law is not obeyed, the factor of deviation is f^H , known as Henry's coefficient :

$$a = f^H \cdot \text{wt.}\% \quad 1.19$$

In a multi-component alloy, the alloying elements affect the activity coefficients of one another. It is possible to find the

* Substances inside the brackets [] and () denote their presence in solution in steel and slag respectively; solid lines under them also denote their presence in steel, e.g., $[\text{X}]$ or $\underline{\text{X}}$ for steel and (X) for slag.

activity coefficient of any component with the help of Wagner's equation.⁴ As for example, the activity coefficient of sulphur in pig-iron is given by

$$\log f_S = \log f_S^S + \log f_S^P + \log f_S^C + \log f_S^{\text{Mn}} + \log f_S^{\text{Si}} \quad \text{etc.}$$

where f_S = overall activity coefficient of sulphur in pig-iron

f_S^S = overall activity coefficient of sulphur in binary Fe-S alloy

f_S^P, f_S^C etc. = activity coefficient representing the effect of the respective elements on the activity of sulphur.

The $\log f$ values for sulphur, nitrogen, oxygen and others are becoming increasingly available from where the overall activity in any alloy system can be easily evaluated.⁵⁻⁷

Further, if the effect of one element on the activity of another is known, the effect of the second on the first can be readily calculated. For example :

Let two solutes A and B with at.wt. ω_A and ω_B be dissolved in liquid iron, the dilution being great. Let it further be supposed that the activity coefficient factor of A is given by f_A^B which depicts the effect of B on the activity of A, where

$$\log f_A^B = x. \% [B]$$

x being any numerical determined experimentally.

Then, the effect of A on B is given by,

$$\log f_B^A = -x. (\omega_B / \omega_A). \% [A]$$

Partition or Distribution law

According to Nernst's Distribution law, if a solute, soluble in two immiscible solvents, is in equilibrium between the two phases, the ratio of the concentrations of the solute in both the phases at a given temperature is a constant provided the dilution is

infinite and the molecular state of the solute in the two phases is the same. It is evident that the activity of the solute in one phase must also bear a fixed ratio to that in the other. This ratio is unity, since the chemical potential of the solute is identical in both the phases.

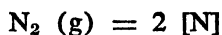
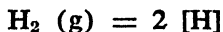
In steelmaking, oxygen is a component of greatest importance which is soluble in two immiscible phases, liquid metal and slag. Since it is not possible to measure the oxygen content of slag, efforts were made to find the distribution or partition constant taking (FeO)-slag and O in pure liquid iron. Although concentrations of both should be in terms of mol fraction, Körber and Oelsen⁸ found a reasonable constant with percentages, the slag being a liquid iron-manganese-silicate :

$$\% (\text{FeO}) / \% [\text{O}] = 450$$

Strictly speaking, the (FeO) contents of all the slags should not bear a fixed ratio as above; for, its amount does not decide the oxidising power of slags. Slags with very different (FeO) contents may have the same oxidising power (*cf.* p. 162, Fig. 4.4a).

Sievert's law⁹

Hydrogen and nitrogen are diatomic in gaseous state but are monatomic in solution in iron. Thus,



According to Sievert's law, the concentration of these gases in solution in iron is proportional to the square root of their partial pressures and is given by the expression of the type.

$$\% [\text{H}] = K \sqrt{p_{\text{H}_2}} \quad 1.20$$

where $\% [\text{H}]$ = concentration of hydrogen in iron

p_{H_2} = partial pressure of hydrogen gas in contact with the metal

K = a constant

K also represents the solubility maximum when the pure gas at 1 atm. is in contact with the metal. The solubility, however, varies with temperature.

Entropy

It is a measure of disorder in a system and is expressed mathematically as

$$dS = dq/T = C_p / T \cdot dT \quad 1.21$$

According to Nernst, the entropy of perfectly ordered crystals at 0°K is zero. The standard values of entropies of substances are generally given at 298 K. Therefore, in case of a chemical reaction, the change of entropy can be evaluated by integrating Eq. 1.21 (cf. Eq. 1.10).

$$\Delta S_T - \Delta S_{298} = \int_{298}^T (\Delta C_p / T) dT \quad 1.22$$

Thermodynamically, a phase transformation is isothermal and reversible. Therefore, the entropy of phase transformation is given by the heat of transformation at the phase change temperature. As for example,

$$S_f = H_f / T_f ; S_e = H_e / T_e ; S_{tr} = H_{tr} / T_{tr} \quad 1.23$$

The final equation will be similar to Eq. 1.11.

Free Energy

According to the Second Law of Thermodynamics, although heat can flow spontaneously from a higher to a lower temperature, the reverse does not happen unless work is supplied from outside. Thus the law puts a limit to the extent to which heat can be converted into work. This apparent loss of work is not due to only the loss of heat in the form of friction, mechanical resistance, etc. The change in the internal energy of the system during the transformation is not wholly available for work and a portion of this energy is absorbed in such a way as to be incapable of performing any external work. The portion of energy available for work may be referred to as *free energy*. It is obvious that if no waste due to friction or loss to surroundings, occurs, this free energy should be capable of performing maximum work possible.

The non-available or bound form of energy, to which the internal energy is *degraded* to a certain extent, is measured by the increase in *entropy* or *disorder* of the system which embodies the thermodynamical irreversibility of the process. This disorder term is the *unavailable* or *bound* energy and this is naturally a product of a potential and a quantitative factor represented by temperature T and entropy S respectively. The heat equivalent of the disorder term is TS . The maximum obtainable work from any heat term H is thus $H-TS$. Free energy G which is a measure of maximum available work at constant pressure is given by,

$$G = H - TS \quad 1.24$$

For any change in the free energy of a system

$$\Delta G = \Delta H - \Delta S.T \quad 1.25$$

When a system is in equilibrium, the driving forces of the forward and reverse reactions are equal. Therefore, the work done in any system at equilibrium is zero. Thus at equilibrium, $\Delta G = 0$.

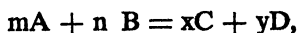
It can be deduced thermodynamically that the free energy change in case of expansion of any ideal gas from a pressure p_1 to p is given by,

$$\Delta G = RT \ln p - RT \ln p_1 \quad 1.26$$

If $p_1 = 1$ atm, then $\ln p_1 = 0$ and therefore $\Delta G = RT \ln p$. Such a condition is known as *thermodynamic standard state* and is denoted by $(^\circ)$ in the exponent. Denoting $\Delta G = G - G^\circ$,

$$G = G^\circ + RT \ln p$$

In case of a general chemical reaction of the type,



$$\Delta G = \Delta G^\circ + RT \ln (a_C^x \cdot a_D^y) / (a_A^m \cdot a_B^n)$$

where ΔG° = total standard free energy change =

$$G_C^\circ + G_D^\circ - G_A^\circ - G_B^\circ.$$

At equilibrium, $\Delta G = 0$ and the equilibrium constant K = the ratio of the activities. Therefore,

$$\Delta G^\circ = -RT \ln k = 4.575 T \log K = -4.575 T \log a \quad 1.27$$

In general, $\Delta G = -RT \ln K + RT \ln (a_C^x \cdot a_D^y) / (a_A^m \cdot a_B^n)$

where K = equilibrium constant

and a_A, a_B, \dots etc. = respective initial activities.

ΔG° value of any chemical reaction indicates whether it is capable of taking place at all. If ΔG° value is negative, the reaction can possibly occur under proper conditions. A positive value denotes the thermodynamic impossibility of the forward reaction and rather a reverse reaction is apt to take place.

Effect of temperature on Equilibrium Constant

Combining Eqs. 1.25 and 1.27 we get,

$$\log K = \frac{-\Delta H^\circ}{4 \cdot 575 T} + \frac{\Delta S^\circ}{4 \cdot 575} \quad 1.28$$

At steelmaking temperatures ΔH° and ΔS° do not change significantly, so that we can write the above equation as,

$$\log K = -\Delta H / 4 \cdot 575 T + \text{constant}$$

The 'constant' term can be evaluated from known value of K at any temperature or from known entropy change.

If K_1 is known for T_1 , then K_2 at T_2 can be found thus :

$$\log K_2 - \log K_1 = \frac{-\Delta H}{4 \cdot 575} \left(\frac{T_1 - T_2}{T_1 \cdot T_2} \right)$$

Free energy in iron alloy¹⁰

Alloys are very dilute solutions of elements in steel and hence it is convenient to refer the free energies to a new standard rather than to mol fractions. The usual standard chosen is unit activity at 1% solution and activity at any other concentration in the region of the validity of Henry's law is equivalent to weight per cent. The difference of free energy between this standard state and that referred to mol fraction, when an element A of atomic weight w is transferred isothermally from pure liquid state to a state of $x\%$ solution in liquid iron, is given by :

$$\Delta G^\circ = 4 \cdot 575 T \log (0 \cdot 5585 / w) \quad 1.29$$

The at. wt. of molybdenum is 95.95. Therefore, from Eq. 1.29, the free energy of dilution of pure liquid Mo in liquid iron is given by :

$$\text{Mo}(l) = \% [\text{Mo}] : \Delta G^\circ = -10.22 T$$

In order to calculate the values from solid-to-liquid states, the free energy of fusion should be taken into account. As for example, in case of Mo

the heat of fusion = 6,600 cal and m.p. = 2,873°K.

Therefore from Eq. 1.23 the entropy of fusion = 6,600/2,873 = 2.29. The desired free energy is obtained as follows :

TABLE—1.2

Reaction	ΔG°	γ_{1873}^{10}
Al(l) = [Al]	-11,700 — 7.70 T^{10}	0.043
C(gr) = [C]	6,400 — 9.7 T	
Cr(s) = [Cr]	4,600 — 11.17 T	1
Co(l) = [Co]	— 9.25 T	1
Cu(l) = [Cu]	9,300 — 9.40 T^{10}	12
Mn(l) = [Mn]	— 9.12 T	1
Mo(s) = [Mo]	6,600 — 12.51 T	1
Ni(l) = [Ni]	— 9.24 T	1
Si(l) = [Si]	-28,500 — 2.23 T^{14}	(0.0077) ¹⁴
Ti(s) = [Ti]	-7,000 — 11.0 T^{10}	0.05
V(s) = [V]	-3,900 — 11.07 T^{10}	0.12
W(s) = [W]	8,400 — 13.79 T	1
Zr(s) = [Zr]	-7,000 — 12.20 T^{10}	0.05
$\frac{1}{2}\text{H}_2(\text{g}) = [\text{H}]$	7,640 + 7.68 T^{10}	
$\frac{1}{2}\text{N}_2(\text{g}) = [\text{N}]$	2,200 + 5.26 T	
$\frac{1}{2}\text{O}_2(\text{g}) = [\text{O}]$	-27,960 — 0.63 T	
$\frac{1}{2}\text{S}_2(\text{g}) = [\text{S}]$	-31,310 + 5.12 T	
$\frac{1}{2}\text{P}_2(\text{g}) = [\text{P}]$	-29,250 — 4.55 T^{12}	
2 CO = CO ₂ + [C]	-34,500 + 31.07 T^{12}	
CO ₂ = CO + [O]	39,540 — 21.38 T	
CO = [C] + [O]	5,040 + 9.69 T	
H ₂ O = H ₂ + [O]	32,200 — 14.63 T^{15}	[O] is rather a.
H ₂ O = 2[H] + [O]	47,480 + 0.73 T	
SO ₂ = [S] + 2[O]	-1,340 — 13.03 T	

$$\text{Mo}(s) = \text{Mo}(l) : \Delta G^\circ = 6,600 - 2.29 T$$

$$\text{Mo}(l) = \% [\text{Mo}](l) : \Delta G^\circ = -10.22 T$$

$$\text{adding, Mo}(s) = \% [\text{Mo}] : \Delta G^\circ = 6,600 - 12.51 T$$

In general, $\Delta G = -RT \ln K + RT \ln (a_C^x \cdot a_D^y) / (a_A^m \cdot a_B^n)$

where K = equilibrium constant

and a_A, a_B, \dots etc. = respective initial activities.

ΔG° value of any chemical reaction indicates whether it is capable of taking place at all. If ΔG° value is negative, the reaction can possibly occur under proper conditions. A positive value denotes the thermodynamic impossibility of the forward reaction and rather a reverse reaction is apt to take place.

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$$\log K_2 - \log K_1 = \frac{-\Delta H}{4 \cdot 575} \left(\frac{T_1 - T_2}{T_1 \cdot T_2} \right)$$

Free energy in iron alloy¹⁰

Alloys are very dilute solutions of elements in steel and hence it is convenient to refer the free energies to a new standard rather than to mol fractions. The usual standard chosen is unit activity at 1% solution and activity at any other concentration in the region of the validity of Henry's law is equivalent to weight per cent. The difference of free energy between this standard state and that referred to mol fraction, when an element A of atomic weight w is transferred isothermally from pure liquid state to a state of $x\%$ solution in liquid iron, is given by :

$$\Delta G^\circ = 4 \cdot 575 T \log (0 \cdot 5585 / w) \quad 1.29$$

The at. wt. of molybdenum is 95.95. Therefore, from Eq. 1.29, the free energy of dilution of pure liquid Mo in liquid iron is given by :

$$\text{Mo}(l) = \%[\text{Mo}] : \Delta G^\circ = -10.22 T$$

In order to calculate the values from solid-to-liquid states, the free energy of fusion should be taken into account. As for example, in case of Mo

the heat of fusion = 6,600 cal and m.p. = 2,873°K.

Therefore from Eq. 1.23 the entropy of fusion = 6,600/2,873 = 2.29. The desired free energy is obtained as follows :

TABLE—1.2

Reaction		ΔG°	γ_{1873}^{10}
Al(l)	= [Al]	-11,700 — 7.70 T ¹⁰	0.043
C(gr)	= [C]	6,400 — 9.7 T	
Cr(s)	= [Cr]	4,600 — 11.17 T	1
Co(l)	= [Co]	— 9.25 T	1
Cu(l)	= [Cu]	9,300 — 9.40 T ¹⁰	12
Mn(l)	= [Mn]	— 9.12 T	1
Mo(s)	= [Mo]	6,600 — 12.51 T	1
Ni(l)	= [Ni]	— 9.24 T	1
Si(l)	= [Si]	-28,500 — 2.23 T ¹⁴	(0.0077) ¹⁴
Ti(s)	= [Ti]	-7,000 — 11.0 T ¹⁰	0.05
V(s)	= [V]	-3,900 — 11.07 T ¹⁰	0.12
W(s)	= [W]	8,400 — 13.79 T	1
Zr(s)	= [Zr]	-7,000 — 12.20 T ¹⁰	0.05
$\frac{1}{2}\text{H}_2(g)$	= [H]	7,640 + 7.68 T ¹⁰	
$\frac{1}{2}\text{N}_2(g)$	= [N]	2,200 + 5.26 T	
$\frac{1}{2}\text{O}_2(g)$	= [O]	-27,960 — 0.63 T	
$\frac{1}{2}\text{S}_2(g)$	= [S]	-31,310 + 5.12 T	
$\frac{1}{2}\text{P}_2(g)$	= [P]	-29,250 — 4.55 T ¹²	
2 CO	= CO ₂ + [C]	-34,500 + 31.07 T ¹²	
CO ₂	= CO + [O]	39,540 — 21.38 T	
CO	= [C] + [O]	5,040 + 9.69 T	
H ₂ O	= H ₂ + [O]	32,200 — 14.63 T ¹⁵	[O] is rather a.
H ₂ O	= 2[H] + [O]	47,480 + 0.73 T	
SO ₂	= [S] + 2[O]	-1,340 — 13.03 T	

$$\text{Mo}(s) = \text{Mo}(l) \quad \Delta G^\circ = 6,600 - 2.29$$

$$\text{Mo}(l) = \%[\text{Mo}](l) \quad \Delta G^\circ = -10.22$$

$$\text{adding, Mo}(s) = \%[\text{Mo}] \quad \Delta G^\circ = 6,600 - 12.51$$

Other such values are given in Table 1.2.

For solutions which deviate sharply from ideality, even the Henry's law does not hold good. In such cases the activity coefficient γ° defining the deviation from Henry's law must be taken into account, e.g.

$$\Delta G^\circ = RT \ln (\gamma^\circ \cdot 0.5585/w). \quad 1.30$$

In the case of gases like hydrogen and nitrogen in liquid iron, they may be assumed to behave ideally. The standard state is a hypothetical 1% solution. At 1 atm. of pure gas, the % solubility is equal to K of Eq. 1.20.

$$\text{Therefore, } \Delta G^\circ = -4.575 T \log a = -4.575 T \log (\text{wt. \%}) \quad 1.31$$

The free energies of reactions of importance to steelmaking are given in Table 1.2. The equilibrium constants of these reactions can be simply obtained by dividing these values with the factor $-4.575 T$. The unknown free energy of a reaction can be obtained from known equations by suitable adjustments (addition and/or subtraction of relevant equations).

Oxygen potential

If two or more phases in a system are in equilibrium, the chemical potential of any component is same throughout. If oxygen gas is in equilibrium with a condensed oxide, the chemical potential of oxygen or, in other words, the oxygen potential in both the phases must be the same. If the oxygen potential in the gaseous phase is more than that in the oxide phase, then the oxygen condenses to form oxide until the potentials are equalised. Conversely, if the oxygen potential in the oxide is more, the oxide decomposes to give out oxygen till the equalisation of the potentials.

Let us consider a three-phase equilibrium at a temperature T between oxygen, a pure metal and its oxide,



Neglecting the vapour pressures of the condensed phases, the equilibrium constant is given by

$$K=1/p_{O_2} \quad 1.33$$

$$\Delta G^\circ = -RT \ln K = RT \ln p_{O_2} \quad 1.34$$

When the equilibrium between the three phases is reached, the oxygen pressure of the vapour phase, the vapour pressure of oxygen above the oxygen-saturated metal and the dissociation pressure of the metal oxide must all be same and equal to p_{O_2} .

Thus, if $\Delta G^\circ = RT \ln p_{O_2}$ is drawn against T , the curves give the variation of the oxygen potential or free energy with temperature. Similar plots can be made for nitrogen, sulphur potentials for nitrides, sulphides and others. The free energy plots of some oxides and nitrides and sulphides are drawn in Fig. 1.2. There are sharp bends in the curves at points where phase trans-

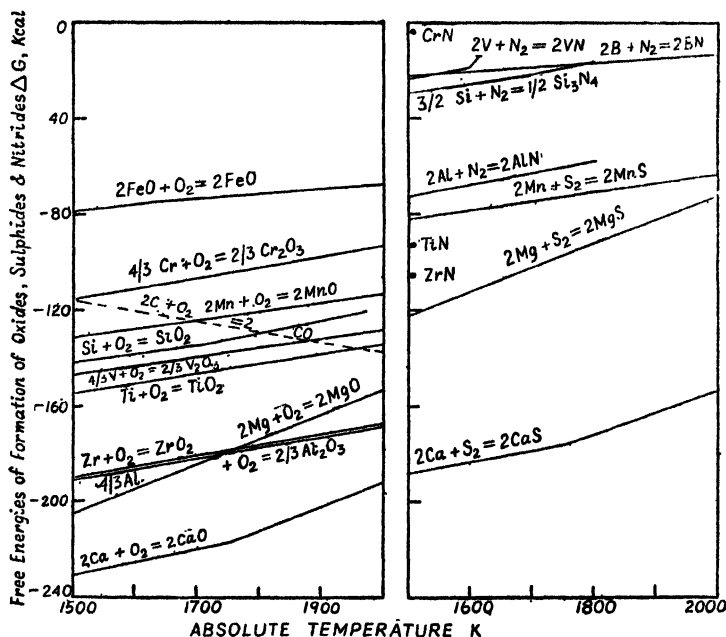


Fig. 1.2—Free energies of formation of some oxides, sulphides & nitrides at steelmaking temperatures.

formations occur. This is because of consequent sharp changes in entropies.

Such diagrams give a clear picture of the stability of the various compounds relative to their sister compounds. The criterion of a chemical reaction taking place is that its ΔG° —value is negative. The less the free energy of formation of a compound (i.e. the greater the $-\Delta G^\circ$), the more stable is the compound. The lower the position of, say, an oxide in the diagram, the lower is its oxygen-pressure and greater is the affinity of the element concerned for oxygen. All these reactions are supposed to take place at an oxygen—(or nitrogen—, sulphur—) pressure of 1 atm. At any given temperature, an element from any lower line is theoretically capable of reducing, i.e. displacing oxygen from any oxide of any line above it; and greater the vertical distance between the two, the greater is the tendency to do so. These diagrams are, however, constructed under standard conditions where all the participating components are in their unit activities. Under different conditions, the free energy is subjected to variations which sometimes are considerable.

It is apparent that such diagrams only theoretically predict the occurrence of any reaction at any given temperature and pressure. They do not in any way foretell whether the reaction can take place at an appreciable rate. The velocity of a reaction which depends upon conditions other than the affinity is a subject that requires the mechanism of reaction or diffusion.

Velocity of homogeneous reaction

It is supposed that a reaction occurs due to collisions between the molecules. Calculations show that the rate of any reaction will be enormous if all the collisions are fruitful. In fact it is not so. The number of collisions which lead to reaction, i.e. the number of *effective* collisions, is only a fraction of the total number of collisions.

The cause of the failure to react on each collision is supposed to be due to the fact that a normal molecule reacts only when it is *activated* by a certain amount of energy, called the *energy of activation*. The reactants are in equilibrium at any given temperature and pressure with the activated molecules. The rate of reaction depends upon the equilibrium constant K^{act} of this

equilibrium. The velocity of reaction is small where this constant is small. The velocity of most reactions increases with temperature since this constant increases with temperature.

Diffusion

The factors which influence heterogeneous reaction rates cannot always be explained by simple kinetic considerations. The reactants present in several phases find opportunity to react only when they come into contact at the phase interfaces. Therefore, apart from the inherent chemical reaction rate, the rate of diffusion of the reactants to the interface and that of the products away from the interface assume importance in the overall velocity of the reaction.

Fick (1855) put forward his well-known *Diffusion Law* that if dn is the amount of a substance flowing in the direction of the concentration gradient of $-dc$ (the minus sign signifies the decrease in concentration along a distance dx) and if S is the cross-section of the upright cylinder which holds the solution and dt the time interval, then

$$dn/dt = -DS \cdot dc/dx \quad 1.35$$

Here D is the diffusion coefficient and is a constant at a given temperature. It is inversely proportional to the size of the molecule and the internal friction of the gaseous, liquid or solid media.

It is assumed that at first a thin apparently saturated non-moving diffusion layer of thickness of the order of 10^{-2} to 10^{-3} cm is formed, through which diffusion of the substance takes place. On this basis Eq. 1.35 can be reformed for practical applications. Use of the equation has been made on p. 193 for calculating the decarburisation rate in the open-hearth process of steel-making.

Oxidation and Reduction

The oxidation of a metal and the dissociation of its oxide are given by Eq. 1.32 from where, in the absence of mutual solubility of the condensed phases and neglecting their partial pressures,

$$K' = p_{O_2} \quad 1.36$$

For every temperature there is a definite pressure of oxygen in equilibrium with the metal and its oxide, known as *oxygen dissociation pressure*— p_{O_2} . It is a function of temperature and increases with increase in temperature. If the p_{O_2} of any gaseous atmosphere in contact with an element is greater than its oxide, the element will suffer oxidation. If it is smaller, no oxidation can take place; rather, the oxide undergoes reduction and oxygen migrates to the atmosphere until the oxygen pressures of the oxide and the atmosphere become identical. This is the basic principle of oxidation-reduction of metals and their oxides. It is true for sulphides, nitrides, etc.

Since steelmaking is essentially an oxidation process, the necessity of supplying oxygen in one form or other is apparent. In the so-called pneumatic processes, the source of oxygen is air, oxygen-enriched air, oxygen-steam or oxygen-carbon dioxide mixture, pure oxygen. In the open-hearth processes, the oxygen is supplied by the oxidising heating gases, apart from direct agents like iron ore, mill-scale (oxides of iron obtained from reheating furnaces).

The determination of the oxygen-pressures of the furnace gases which are the products of combustion of carbon monoxide, hydrogen, hydrocarbons and other carbonaceous fuels, is not simple. However, approximate calculations can be made from CO and CO₂ or H₂ and H₂O values in the furnace atmosphere. The oxygen pressure increases with the amount of CO₂ or H₂O and it can be estimated from CO₂/CO or H₂O/H₂ ratios with the help of the free energy values.

Example

To find the oxygen pressure of a mixture of

- (i) 90% CO₂ & 10% CO (ii) 50% CO₂ & 50% CO
at 1,600°C = 1,873°K.



Dividing by — 4.575 T , $\log K = 29,500/T + 9.1$

At 1,873°K, $K = p_{\text{CO}}^2 \cdot p_{\text{O}_2} / p_{\text{CO}_2}^2 = 2.34 \cdot 10^{-7}$

Case (i) $p_{\text{CO}} = 0.1 \text{ atm}$ & $p_{\text{CO}_2} = 0.9 \text{ atm}$

$$p_{\text{O}_2} = 1.78 \cdot 10^{-5}$$

Case (ii) p_{CO} and p_{CO_2} each 0.5 atm

$$p_{\text{O}_2} = 2.34 \cdot 10^{-7}$$

Fig. 1.3 shows the graphical relationships between CO_2/CO & $\text{H}_2\text{O}/\text{H}_2$ mixtures and their oxygen pressures at $1,600^\circ\text{C}$. The figure includes the oxygen contents of liquid iron under the corresponding atmosphere.

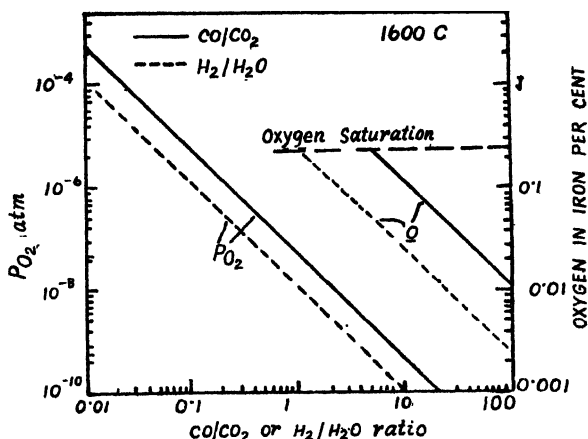
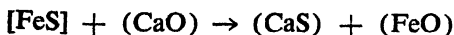
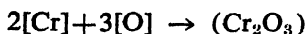
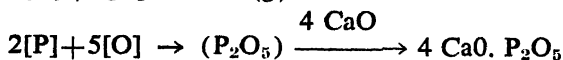
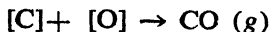
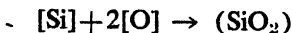


Fig. 1.3—Calculated relationship between CO_2/CO & $\text{H}_2\text{O}/\text{H}_2$ mixtures and their oxygen pressures at $1,600^\circ\text{C}$. The oxygen contents of liquid iron under these atmospheres are also shown as $\underline{\text{O}}$.

The reactions that take place during refining of steel are :



etc.

etc.

In general, $[\text{M}] + [\text{O}] = (\text{MO}) : K = a_{\text{MO}} / (a_{[\text{M}]} \cdot a_{[\text{O}]})$

It is apparent that the oxidation will be more complete, the greater the value of K itself, higher the oxygen input, i.e. $a_{[O]}$ ($[M]$ may be deemed as more or less constant in steelmaking processes) and lower the value of a_{MnO} . Since the products of oxidation except CO are generally insoluble in iron they go over to form the slag and the oxidation is facilitated if their oxides are held in a state of low activity in the slag. This is very apparent in Thomas or basic bessemer process where the removal of phosphorus is delayed until enough lime dissolves in the slag and binds the oxidised element as calcium phosphate. Normally, in acid Bessemer carbon should be oxidised before manganese. But the latter reacts earlier since its oxide MnO forms manganese silicate with the consequent low activity. In basic processes, the initial manganese silicate formed reacts with dissolving lime which releases some MnO and thus increases its activity. This increase retards further oxidation or rather some manganese is reduced or *reverted* back to the metal.

In short, the oxidation of any element increases with decreasing activity of its oxide and its reduction is facilitated with increasing activity of the oxide and/or with the decreasing activity of the element as in the formation of an alloy with another element.

Eq. 1.37 can also be called *deoxidation reaction* since the *residual* oxygen in steel after refining is removed by deoxidisers like Si, Al and sometimes Zr, Ti, etc. If the activity of their oxides is taken as constant, Eq. 1.37 can be written as :

$$K' = \% [O] \cdot \% [M] \quad 1.38$$

The lower the value of K' , the greater is the deoxidising action.

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STEELMAKING PROCESSES

Pig iron obtained from the blast furnace contains, depending upon the raw materials used and the manner of operation of the furnace, varying amounts of mainly carbon, silicon, manganese, sulphur, phosphorus. The range of these elements in the iron is generally : 3.5—4.5% C, 0.2—2.5% Mn or more, 0.3—4.0% Si, 0.04—0.15% S, 0.02—2.0% P or more. Such a high content of carbon renders iron brittle and incapable of being rolled, forged or shaped. Phosphorus, silicon and sulphur are mostly undesirable for mechanical treatment or for mechanical properties of the finished steel. Steel may contain anything up to 1.7% C and varying amounts of other elements which may be deliberately added or retained in order to impart to it certain physical and mechanical properties demanded from the services to which it is put. S, P, N are generally kept as low as economically possible but sometimes higher contents of these are desired for better machinability, hardness, etc.

It is necessary to remove carbon and other impurities from pig iron to a desired extent in order to obtain steel. Most of these elements can be and are removed by oxidation. Except the oxidation products of carbon (CO) and a little of SO₂ which are in gaseous state, other oxides of elements are removed in the slag together with some iron oxide which is formed due to unavoidable oxidation of a part of iron. The oxidising agents used are air, oxygen, gaseous products of oxidation of fuels, ores, mill-scale (oxidised surface of blooms, ingots, etc., from rolling mills) and the like.

There are various processes by which the oxidation is performed and steel is made. These processes have been devised to provide a controlled supply of oxygen to molten iron for the purpose of refining. The choice of the method depends upon the nature of raw materials available, economy, products and properties desired. Steelmaking has been divided broadly into (i) acid and (ii) basic processes. Whereas carbon, silicon and

manganese can be removed with efficiency either by acid or by basic processes, the removal of sulphur and phosphorus requires lime to form a basic slag. It is imperative that the refractory lining of the steelmaking vessels should be acid in acid processes and basic in basic processes, since otherwise the slag and lining would react thereby changing the character of the slag and destroying the lining rapidly.

The following are the important processes used for steel-making :

Pneumatic Processes

In these processes air, air-oxygen, oxygen-steam, oxygen-carbondioxide or pure oxygen is blown through and/or on the surface of molten iron in order to effect the oxidation of the foreign elements. It is necessary that sufficient heat be supplied to the molten pig-iron, as oxidation or *refining* proceeds, to maintain it in a molten state and finally raise it to steelmaking temperatures 1,550–1,650°C. Pig-iron is obtained generally between 1,300–1,400°C from the blast furnace in a molten state because carbon (and to a little extent other impurities) lowers the m.p. of iron (1,535°C). The m.p. of the molten iron rises continually with the removal of carbon and if heat is not supplied simultaneously the metal may freeze. Such heat is obtained mainly from exothermic heats of reaction of silicon in acid and of phosphorus in basic pneumatic processes. If air alone is blown through, its inert constituent nitrogen, during its travel through the molten bath into the atmosphere, extracts considerable useful heat from the system.

The refining time and the nature of the products depend considerably upon the manner the oxidation is carried out. The different methods of pneumatic steel production are discussed briefly in the following sections.

Acid bessemer process

Molten pig is taken in 20-50 tons capacity converters lined with acid silica bricks and blown with air, through a detachable bottom fitted with refractory tuyeres, at pressures 20-30 psi. The pear-shaped vessel, as shown in Fig. 2.1a, is mounted on two trunnions on which it can be tilted horizontally during pouring liquid iron

and moved to vertical position when blowing. In order to produce sufficient heat, enough silicon should be present whose exothermic heat of reaction raises the temperature of the bath to the neighbourhood of $1,600^{\circ}\text{C}$. Too much of silicon overheats the metal and coolants like steel scrap are used or steam is mixed with the air blast which has a cooling effect due its endothermic heat of dissociation. However, mill-scale or iron ore are more efficient coolants in view of the fact that reduction of these oxides to iron consumes more heat than required to melt solid metal. The composition of hot metal for a good blow is given in Table 2.1.

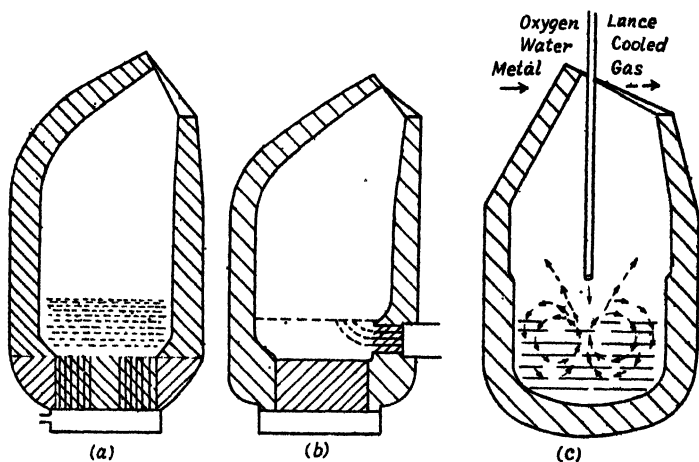


Fig. 2.1—(a) Conventional bottom-blown converter (b) Side-blown converter (c) Top-blown oxygen converter.

The oxygen required for producing one ton of bessemer steel is about 65m^3 or 300m^3 of air. Aerial oxygen coming out of tuyeres oxidises iron at first to FeO and then reacts directly or indirectly in the form of FeO with silicon and manganese producing exothermic heat which rapidly increases the temperature of the bath. The burning of Si and Mn, which takes place in the beginning, produces a short flame. As their concentrations decrease and the temperature simultaneously increases, the oxidation of carbon to monoxide begins and a long flame emanates from the mouth of the converter because of burning of CO with atmospheric oxygen. The products of oxidation form acid slag

of mainly FeO , MnO , SiO_2 with little impurities from the converter lining (CaO , Al_2O_3). CO is a gas and escapes.

The oxygen content of iron is kept low as long as sufficient carbon is present and increases as carbon falls.

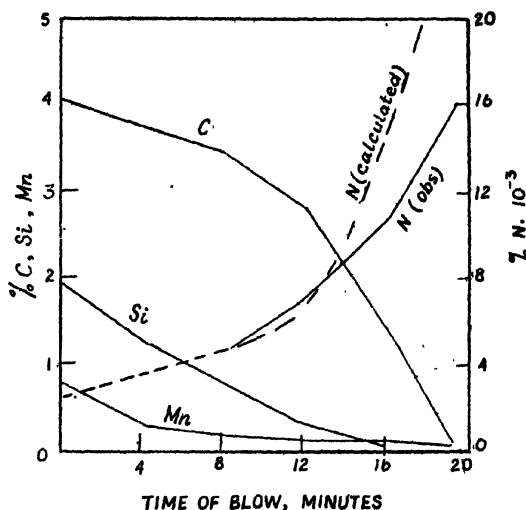
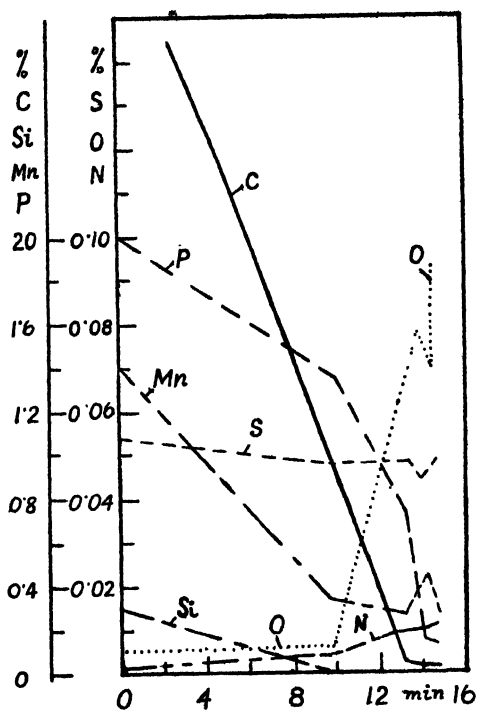


Fig. 2.2—Compositional changes during a typical Acid Bessemer blow. The calculated nitrogen variation is shown by the dotted line. (By permission from 'The Physical Chemistry of Metals' by L. S. Darken & R. W. Gurry. Copyright 1953. McGraw-Hill Book Co.)

In order to obtain a uniform product the proper control of the end point becomes essential since uniformity of products depends greatly upon the oxygen content of steel. The change of composition during a bessemer blow is shown in Fig. 2.2¹. The nitrogen curve shows a steep rise during the latter period of the blow. Fig. 5.12 shows the amount of dissolved oxygen as a function of carbon content in a normal bessemer blow. Below about 0.05% C the curve rises upwards sharply, indicating the importance of proper control at the end of the blow; otherwise considerable oxygen pick-up by steel would take place and would need for its removal more deoxidisers to obtain clean steel. Below about 0.01% C, further oxidation leads only to burning of iron to its oxides.



TIME OF BLOW.

Fig. 2.3—Compositional changes during a typical Thomas or Basic Bessemer blow.

In bottom-blown acid Bessemer process the fluidity and composition of the slag are of extreme importance. A fluid or watery slag is very disadvantageous and is avoided not only because such a slag flows with the metal into the casting ladle but also for the fact that a fluid slag is accompanied by *slopping*, i.e. considerable amounts of metal and slag are thrown out of the converter. It is, therefore, intended to produce the so-called 'dry' slag. This slag is also more or less 'inactive,' i.e. it does not take part in the slag-metal reactions in contrast to the open-hearth slags which are fluid and metal and slag can react to reach equilibrium. A Si/Mn ratio above 2 in the pig iron gives such a slag. A typical analysis of the slag is given in Table 2.1.

TABLE-2.1

Process	Composition of Iron & Steel in per cent					Composition of Slag in per cent							
	C	Si	Mn	P	S	CaO	MgO	SiO ₂	MnO	FeO	P ₂ O ₅	Al ₂ O ₃	Fe ₂ O ₃
Acid Bessemer Iron Steel	3.5-4.0 0.06	1.8-2.5 Trace	0.7-1.0 0.05	0.04 max. 0.05	0.04 max. 0.05	1-2	1.0	60-70	10-20	10-20		2-5	2
Basic Bessemer Iron Steel	3.0-3.5 0.02-0.05	0.4-0.8 Trace	1.0-2.5 0.15-0.20	1.7-2.2 0.05-0.05	0.1 max. 0.05	45-55	2-5	5-10	2-5	8-15	15-22	2-3	2-7
Basic Openhearth Iron Steel	3.0-3.5 Spec.	1.0 max. 0.05	1.0-2.5 Spec.	0.2-1.2 0.03	0.07 max. 0.03	40-50	2-5	15-22	5-10	10-20	2-6	3	2-5
Acid Openhearth Iron Steel	3.0-4.0 Spec.	1.5-2.5 Trace	2.5-3.0 Spec.	0.04 max. 0.04 max.	0.04 max. 0.04 max.	2-10	1.0	50-60	8-20	8-15		2	
Acid Electric Iron Steel	Spec.	Spec.	Spec.	0.025 max. 0.025 max.	0.025 max. 0.025 max.	2-10	1.0	50-60	12-20	8-15		1.0	
Basic Electric-Iron 1st Slag Steel	3.0-4.0 Spec.	0.2-1.0 Trace	1.5-2.5 0.25-0.5	0.15-0.5 0.015-0.0	0.04-0.08 0.025	35-50 50-65	4-8 4-10	10-25 15-25	5-10 0.1	0.5 8-20	0.2-1.1 0.1	1.5-3.0 0.5-3.0	1.5-7 Nil
LD-Iron Steel	3.0-4.0 0.05-0.15	0.2-1.0 Trace	1.5-2.5 0.25-0.5	0.15-0.5 0.015-0.0	0.04-0.08 0.025	35-50	2-5	10-15	9-12	17-21	1-5	2-4	
Kaldo-Iron 1st Slag Steel	3.0-3.7 0.1-1.0	0.2-0.4	0.6-0.9 0.2-0.3	1.7-2.0 0.1-0.3	0.03-0.08 0.015	50-55	2.5-3.5	7-8	2.5-3.5	7-13	18-20		
2nd Slag Steel	0.1-0.5		0.1	0.03	0.015					5-8	15		
Rotor-Iron Steel	3.5 0.15	0.4 Trace	1.4 0.25	1.8 0.03	0.06 0.015	45-55				10-15	18-20		

Fluid or 'wet' slag is produced when Si|Mn is lower than 2 or so, or when the metal is overoxidised giving large amount of FeO which fluxes the 'dry' slag. In case of wet slags, the degree of oxidation of bath is difficult to control. In Workington² high manganese pig is usual (1.8—2.3% Si and 1.0—1.3% Mn). Such an iron has been used satisfactorily through proper control of blow although it produces wet slag.

Phosphorus and sulphur are generally not removed by the acid slag. The use of natural air introduces nitrogen which amounts to 0.010—0.017% in the finished steel. The consequent strain-ageing and strain hardening effects limit the application of acid bessemer steel, specially for sheet and pipe products. It is possible to produce very low nitrogen steel of the order 0.002% if, instead of natural air, a mixture of steam|oxygen is blown. The mixture has however to be thermally equivalent to natural air and a 50|50 or 40|60 per cent of steam|oxygen mixture has generally been found to be suitable.

Yocom³ has developed a method of dephosphorising acid bessemer steel from 0.08—0.09% P to about 0.02—0.04% P. This has been achieved by pouring the liquid converter steel on to a suitable low-melting mixture of small sized lime (CaO), mill-scale, fluorspar (CaF₂) and soda ash (Na₂ CO₃). This treatment combined with oxygen|steam blowing furnishes open-hearth quality steel with low phosphorus and nitrogen.

The temperature of steel can be increased (when blow is cold or scrap is desired to be melted) by tilting the converter slightly from the vertical position, so as to expose a few tuyeres (oblique blowing). The air coming through these exposed tuyeres burns the CO evolved from bath to CO₂ inside the converter and the great heat then generated helps to increase the temperature and melt the scrap. The same can be partly achieved in side-blown converter (Fig. 2.1b). In this type nitrogen absorption is much reduced. The reason will be apparent from the discussions on pp. 388-89.

Thomas or Basic Bessemer Process

The name of the process suggests that steel is produced from pig-iron under basic conditions. In Germany it is exclusively known as Thomas Process. The vessel and the accessories are

similar to those in the acid process except that the lining and bottom are made with rammed burnt dolomite $\text{MgO} \cdot \text{CaO}$, (mixed with tar to act as bond). In the acid process the slag is produced from the oxidation products of Si, Mn and Fe, whereas in the basic, the added lime, together with the products of oxidation, i.e. SiO_2 , MnO , FeO , P_2O_5 etc. forms a basic slag which is capable of holding phosphorus and sulphur. The exothermic heat of phosphorus oxidation is the main supplier of heat for maintaining the metal in fluid state and also for raising it to the steelmaking temperatures. A typical analysis of pig-iron for basic converter and the slag formed is given in Table 2.1.

The variation of the concentrations in the conventional practice of blowing natural air is shown in Fig. 2.3⁴, the order of removal of the impurities being Si, Mn, C and P. It is probable that these variations are due to the changes in slag character. On the introduction of air, silicon and manganese are converted to their respective oxides, the rate of oxidation of Mn being slower than in the corresponding acid process. The initial slag formed is an iron-manganese-silicate and is therefore acidic. Lime does not dissolve at first, the exothermic heat of oxidation of low silicon being not enough to bring CaO into solution. This acid slag binds MnO very strongly (as silicate) which is shown by the higher (MnO) content of this initial slag. The oxidation of carbon to CO also takes place, at first slowly (as long as much of Si is still there) and then rapidly.

The phosphorus decreases upto about 75% of its original concentration in the first 10-14 minutes when most of the carbon has been removed. After this period the dephosphorisation is very rapid. (The mechanism of dephosphorisation has been dealt with on pp: 95-114). This period of blow which is the beginning of real dephosphorisation after the carbon removal and continues to the end of the process, is called the 'after-blow' and lasts for 2-3 minutes. Usually, at this time the blow is stopped, samples taken for visual estimation of P and subsequently reblown for a pre-determined number of seconds to bring the phosphorus content from about 1% to 0.05%. The demand of phosphorus for oxygen during this period is so large that it reduces FeO more rapidly than FeO is formed by aerial oxidation. Thus, a considerable deoxidation takes place with a decrease of metal oxygen

and a consequent reduction of MnO (because of lowering of oxygen potential of metal and slag). After the completion of dephosphorisation, the slag again becomes richer in FeO and the $[\text{Mn}]$ decreases due to oxidation and adjusts itself to equilibrium condition with the slag. This behaviour of Mn is shown by the 'hump' in the later periods of the blow (see Fig. 2.3).

The phosphorus removal is favoured by high oxygen in the metal, high FeO and lime in the slag and by low temperature. The temperature can be controlled by addition of scrap while judicious use of mill-scale and ore helps both as coolants as well as oxidisers of slag and metal.

The removal of sulphur is favoured by low FeO and high lime content of slag. Sulphur removal rather starts during dephosphorisation, probably because of far-reaching deoxidation of metal and slag during this period and the dissolution of lime with the formation of highly basic slag.

Nitrogen increases steadily during the blow and very rapidly during the dephosphorisation period. Nitrogen absorption upto 0.015% is facilitated during this period because of rapid rise in temperature and the prevailing reducing conditions. Oxide coolants help considerably in keeping down the nitrogen in the metal both because of lower temperature and their oxidising actions (*cf.* p. 387). The method of keeping down the nitrogen is to charge iron ore, mill-scale and limestone, instead of scraps as coolants, producing thereby a steel with nitrogen as low as 0.010% or even less (HPN^5 , LNP^6 processes, Fig. 2.4⁷). With the same coolants and air enriched with upto 30-35% oxygen, nitrogen can be brought down to 0.005%, and the metal temperature can also be higher. Further discussions are on pp. 386-90.

After the initial blow with oxygen-enriched air, the subsequent finishing blow can be performed by oxygen-steam mixture. A large amount of scrap ($\sim 15\text{-}20\%$) can be used and end nitrogen is about 0.004%. In order to produce steel with still lower nitrogen the use of air has to be excluded. Blowing with oxygen|steam leads to nitrogen values of only 0.002% (*cf.* Fig. 2.5⁸, also p. 391). This value is somewhat lower than in open-hearth varieties and such steel can be used for ship plates and deep drawing purposes. A mixture of oxygen|carbon dioxide

has also been successfully sued. The use of oxygen in all these processes permits the utilisation of scrap.

It must, however, be noted that in all these processes the phosphorus is of the order of 0.04—0.05%. This is rather on the high side for very special types of steel and in order to bring it down to about 0.025%, double slagging is resorted to (*cf.* p. 288).

The proper control of the end-point is very important because an over-oxidation leads to excess oxygen in steel causing the usual defects. The oxygen in Thomas steel is usually less than that in open-hearth for the same C-content if the blowing is stopped at the proper moment, i.e. when iron oxidation starts afresh after dephosphorisation.

Great advances have been made in recent years to improve Thomas steel quality, specially regarding its nitrogen content. A great disadvantage of this process is the delayed dephosphorisation occurring after the removal of carbon has been complete. Such a steel will evidently have to be recarburised if higher carbon-content is desired. In basic open-hearth, phosphorus removal takes place before decarburisation and therefore tapping can be done at any carbon level if other specifications are within limits. This avoids excessive oxidation of the metal and therefore use of heavy deoxidisers and resultant excessive non-metallic inclusions. Further, due to the profuse carbon boil in open-hearth the hydrogen (and nitrogen) is removed considerably by the washing action of the evolved carbon monoxide.

L. D. Process⁹⁻¹¹

The new process of top-blowing of iron in basic converters (Fig. 2.1c by 99.5% pure oxygen at supersonic speed through water-cooled lance has revolutionised steelmaking. This process has metallurgically more in common with the basic open-hearth, although the layout and plants and accessories are similar to any Thomas works. It was developed at Voest in Linz, Austria where the pig-iron produced from local ores contains phosphorus—0.2% and is not suitable for conventional Thomas blow. The process, known universally as LD, has made rapid strides because of lower installation investment in comparison to open-hearths of the same capacity, abundant existence of low phosphorus ores, flexibility of use of various types of pig-iron, possibilities of using

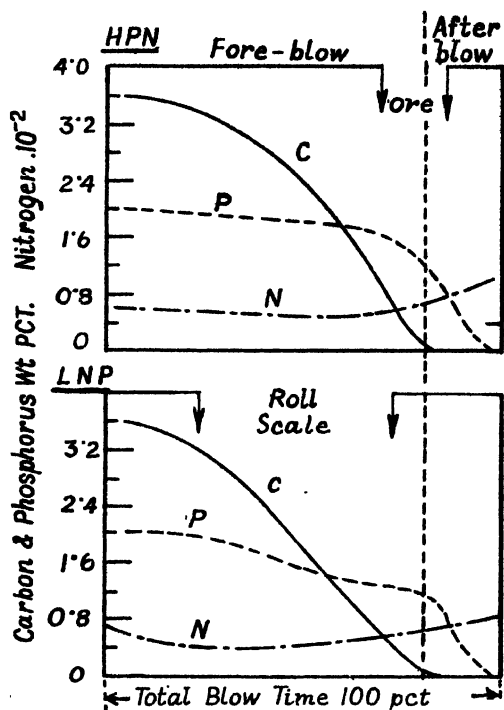


Fig. 2.4—Compositional changes during HPN & LNP blows.
(From Blast Furnace & Steel Plant, Pittsburgh, Pa.)

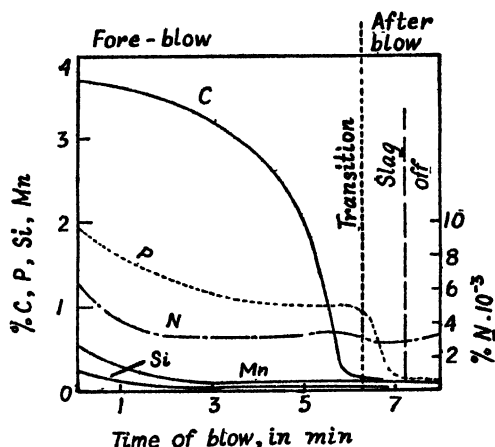


Fig. 2.5—Compositional changes during a typical oxygen/steam blow.
[The elements underlined denote their percentages in steel.]

of scrap even upto 30-33% and very low nitrogen in finished steel. The time of blowing is however more (about 45-60 minutes depending upon the capacity). Even 300 ton converters are feasible and are being tried. The impingement of oxygen on molten iron produces intense heat (about 2,500-3,000°C is reached in the zone around the place of impingement) and oxidises iron to ferrous and ferric oxides which rapidly liquefy and bring the lime in solution to form a highly reactive liquid basic slag, capable of phosphorus removal. Due to the absence of turbulence as in bottom blown converters, the reaction of carbon with iron oxide in LD process is sluggish and the reducing action of carbon is not so pronounced. This helps the bath to maintain a higher oxygen potential for early dephosphorisation. It is, therefore, possible to effect a dephosphorisation before complete decarburisation (in contrast to Thomas process) and steel may be obtained at any desired carbon level by stopping the refining at the proper moment. The intense heat evolved due to use of almost pure oxygen enables additions of a large amount of scrap and ore as coolants (ore acts also as oxidising agent). Nitrogen content is kept as low as 0.003-0.005%. In case of high silicon iron, it may be necessary to slag off the initial acid slag and add more lime for obtaining the required basicity. A typical blow is shown in Fig. 2.6.¹⁰

The other new processes for basic steelmaking with oxygen for refining are the Kaldo and the Rotor. Both make use of rotary vessels and oxygen lancing. Rotation of the vessel creates a stirring action in the bath (which is absent in L.D. process) as well as helps in the conservation of heat because the CO evolved during decarburisation burns in the vessel to form CO₂ with the evolution of large amount of heat which heats up the lining not in contact with the bath and then subsequently gives up the heat to the metal when it comes into contact with the heated portion of the lining during rotation.

Kaldo Process^{10 12 24}

This process was originally started at Domnarvet, Sweden in 1956 with the intention of refining high-phosphorus iron by oxygen. It uses a rotating basic refractory-lined vessel. The design is shown in Fig. 2.7²⁴. The vessel is inclined at an angle of 17-20° and possesses two running rings which rest on four supporting

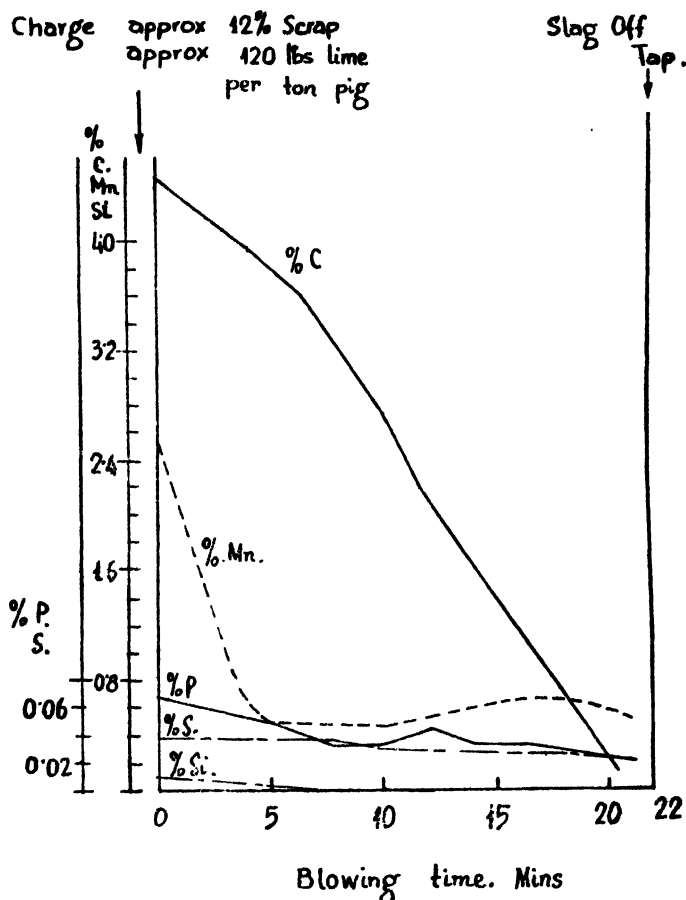


Fig. 2.6—Compositional changes during an LD blow.
(By courtesy of Steel & Coal).

wheels. It can be turned round two trunnions and brought to various positions for charging and tapping. The original 25-30 ton vessel has inside diameter 2.3m when newly relined and is 5.5m in length, corresponding to a volume of 0.65m³/t of steel.

The inclination has a two-fold purpose. One is the overall larger volume in the tilted than in the horizontal position, the other being to cover more than half of the back wall, so that no portion of it may be overheated without being cooled down by molten metal during rotation. The rotation has also three-fold purpose : one is the cooling of the exposed overheated lining by

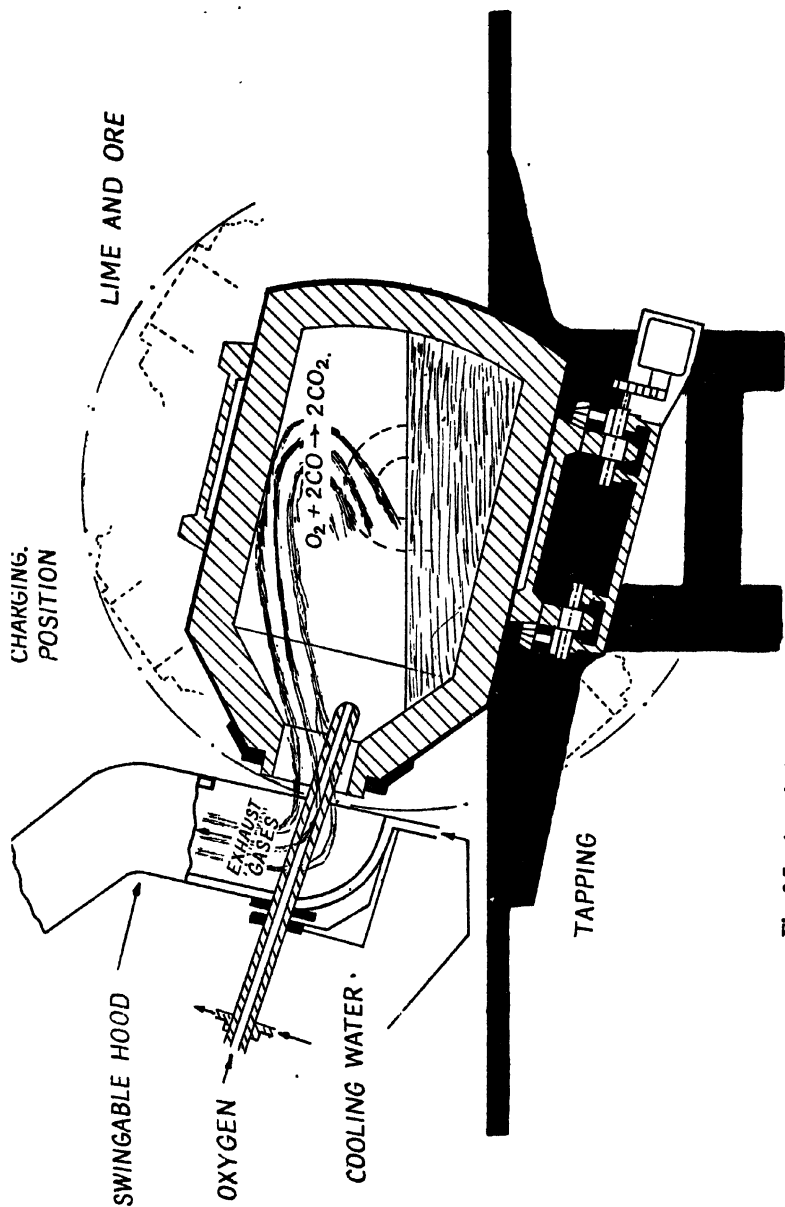


Fig. 2.7—A typical Kaldor vessel. (By courtesy of Iron & Steel Engineer).

molten metal, the second the creation of necessary stirring for better diffusion and slag-metal reaction and thirdly (which is a corollary of one), the absorption of heat from the overheated lining by the metal for melting scrap and using ore for oxidation whose reaction with carbon in metal is highly endothermic. Thus, ore and scrap not only increase metallic yield but also act as coolants to prevent overheating.

The temperature of the outgoing gases is a measure of decarburisation rate. This is because if large amount of CO is evolved, some unburnt gas will go out at the exit (since oxygen supply is limited and constant) and burn outside increasing the exhaust temperature. On slowing down the rotation speed, carbon reaction will subside (for reasons see p. 218), CO will burn completely inside the vessel and the exhaust temperature will fall. Thus, from experience and close study of this temperature, the decarburisation rate can be controlled at will by altering the speed of rotation of the vessel. The carbon removal can also be slowed down by varying the angle of impingement of oxygen on the bath. A flatter angle will play more on slag and less of carbon in the metal will get oxidised.

The oxygen is supplied through a water cooled lance at a pressure of ~ 3 atm and directed at the bath at an angle of $25-35^\circ$ depending upon the operating conditions.

In Domnarvet, the pig iron resembles basic Bessemer variety. After charging of pig iron, the slag formers and coolants (lime and ore) are added and the oxygen blow starts. After the main removal of Si and some Mn, the carbon oxidation starts along with oxidation of a further amount of Mn which remains more or less constant when C—oxidation continues vigorously. The vigour of the carbon boil is kept under control by slowing the rotation and blowing oxygen at a flatter angle. This also enables a more complete combustion of CO and hence effects a greater heat economy. Phosphorus oxidation continues along with carbon removal. The slag however melts much later, when the temperature as well as the dephosphorisation rate are high. This can be easily recognised from the increase in motor load (40-50% increase) since the semi-fluid slag sticks to the lining during rotation. A sudden or gradual decrease in the load suggests the melting of slag and no layer sticking. This usually

happens at 0.5% P. At this stage, there is a manganese reversion from slag to bath (as in Thomas process) and the iron content of slag is also low. Further injection of oxygen is necessary for removal of phosphorus and both Mn and Fe in slag rise. The first slag off is usually done at 0.1% P. At this stage, carbon may vary within wide limits according to rotation speed, amount of ore charged and angle of oxygen injection. However, usually it is done at 0.2–0.3% C for low carbon steels. For higher C—steels the slag off is usually done at 0.2–0.3% P and 1–1.5% C depending upon the desired final contents. In order to minimise lining erosion it is desirable to attempt a late dephosphorisation and, therefore, a late liquefaction of slag. As the slag liquefies and (Fe)-slag increases, the attack on the refractory increases enormously. The rich phosphate first slag contains 18–20% P_2O_5 ; 51–54% CaO; 7–8% SiO_2 ; 2.5–3.5% MgO; 2.5–3.5% MnO and 8–10% Fe. The slag bulk is 280 Kg/t of pig.

About 80% of this slag is usually drained off and a new slag made with additional lime and ore. It is further blown with

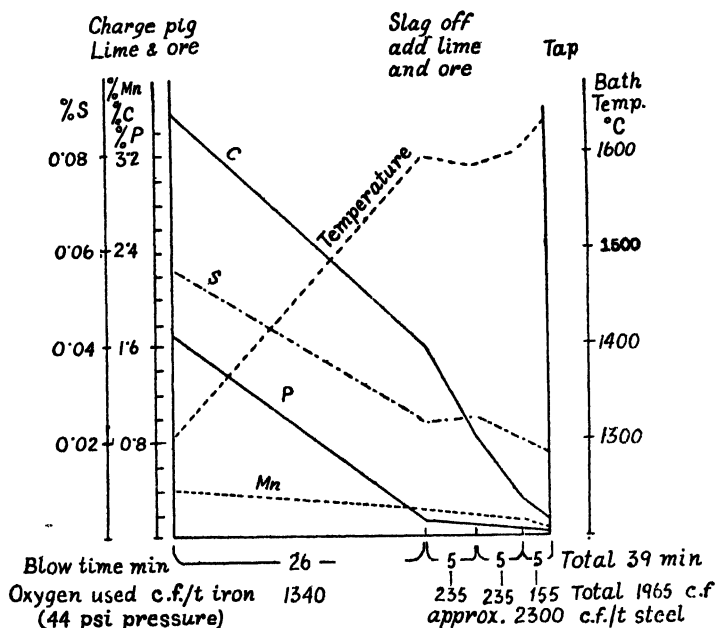


Fig. 2.8—Compositional changes during a Kaldo blow.
 (By courtesy of Steel & Coal).

oxygen to attain the desired P & C contents. Tapping temperature is 1,620-1,650°C.

A second slag off may be necessary to attain very low phosphorus $\sim 0.02\%$ P max. Typical compositional changes during a Kaldo heat is shown in Fig. 2.8.¹⁰

The bulk of sulphur is removed at the first slag off when (Fe) is low and basicity is high. The total desulphurisation in Kaldo process is between 60-80%. When very low sulphur is required the first slag off may be done at high C-content since low (Fe) is associated with high-carbon. We will see later (*cf.* p. 316), a high (Fe)-slag hinders sulphur removal.

The Kaldo process is very flexible and almost any type of steel can be produced from any variety of pig. Even acid steels can be made when the vessel is lined with acid bricks. Both low and high carbon steels can be produced with low P, S and N. Low carbon electrical steels and high carbon tool steels are comparable to any produced by other processes. The tests show very good impact strength and non-ageing and cold working properties.

*Rotor Process*¹³

The Rotor process was originally developed in Oberhausen for pre-refining of pig-iron for use in the open-hearth. The vessel is a cylindrical one, placed horizontally with an opening on each end, for charging and escape of waste gases, as shown in Fig. 2.9. It rotates slowly with a speed of 0.1-0.5 r.p.m. The lining is of magnesite bricks coated with tar-dolomite. It is charged when hot with scrap and ore and subsequently liquid iron is poured in. Oxygen is blown through two lances. The water-cooled primary lance dips in the molten metal and the oxygen both oxidises and stirs the metal. The secondary lance is placed above the charge and the oxygen in this case can only burn the metal and slag whipped up by the turbulence created by the primary jet. The great amount of heat from burning of CO heats up the lining which is cooled down by the metal when it comes in contact during rotation. This rapid heating together with the oxidised iron helps in the early creation of a liquid basic oxidising slag which causes acceleration of dephosphorisation.

This process can be used for any range of phosphorus content of

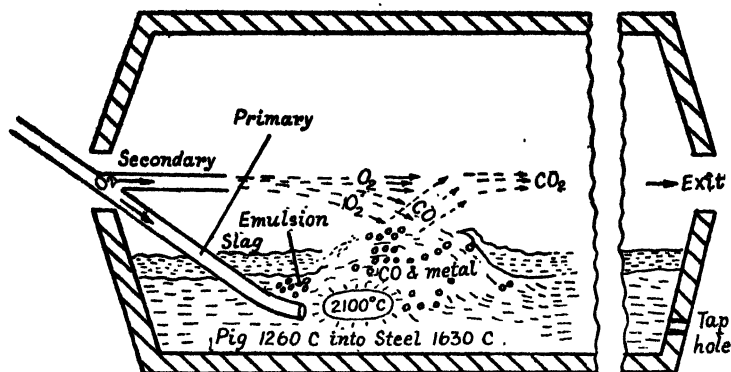
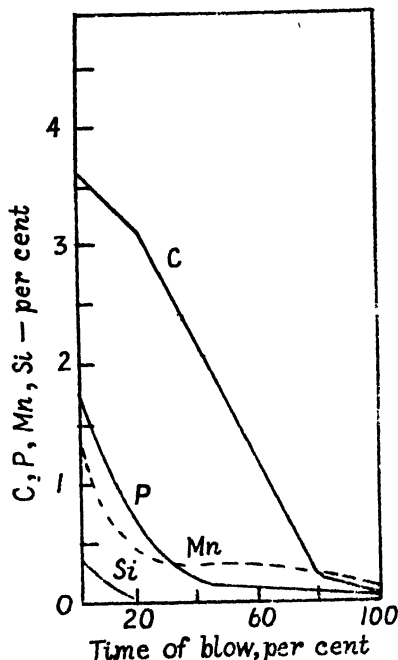


Fig. 2.9—A Rotor vessel (schematic).

Fig. 2.10—Compositional changes during a Rotor blow.
(R. Graef, Stahl und Eisen, 77, 1957, 17).

pig-iron. For high phosphorus iron, a double slag technique has to be adopted, as in the Kaldo process. Dephosphorisation precedes decarburisation and their relative rates are shown in

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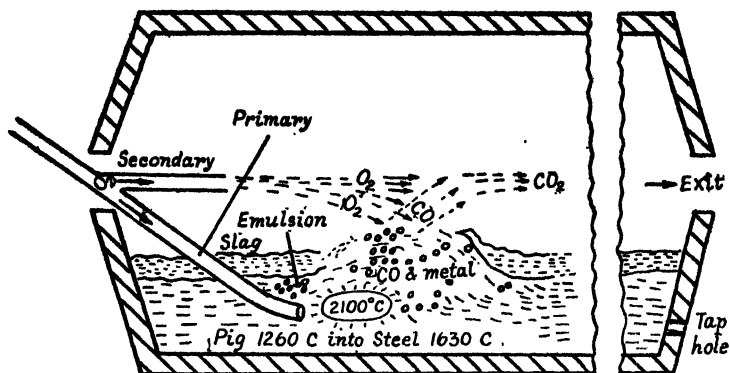
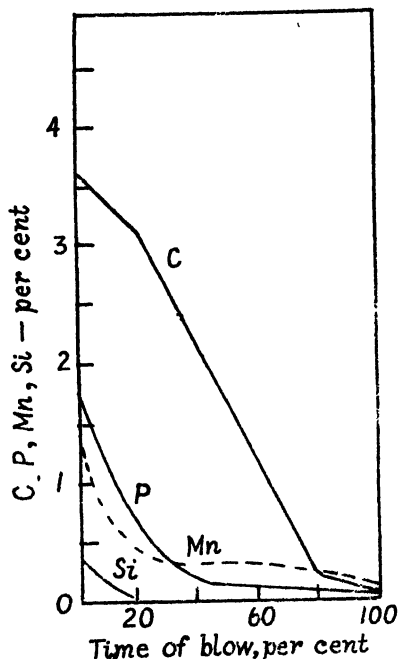


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pig-iron. For high phosphorus iron, a double slag technique has to be adopted, as in the Kaldor process. Dephosphorisation precedes decarburisation and their relative rates are shown in

Fig. 8.15. The rates for L.D. and Thomas processes with normal and oxygen-enriched air are also shown. A Rotor blow with Thomas pig is shown in Fig. 2.10.¹³

A new type of vessel, still in the experimental stage, is elliptical in shape and because of unequal radius inside the vessel helps in creating a great turbulence and stirring of the bath and slag. This thorough mixing should help in the slag-metal reactions.¹⁴

The other finer improvements in the oxygen blowing processes are the use of finely powdered or small pieces of lime, injection of lime together with the oxygen blast (LD-AC, OLP, cf. Fig. 2.11)^{10 15-17} In Thomas process, in order to attain low

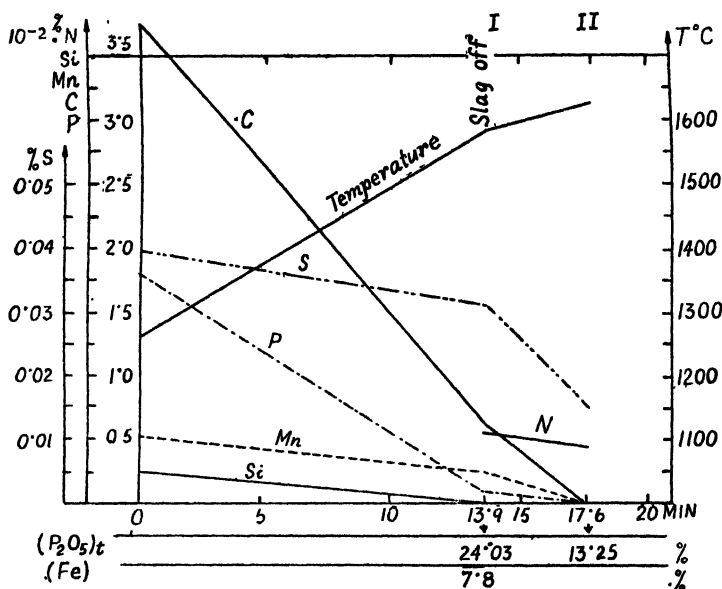


Fig. 2.11—Compositional changes during an LD-AC blow
(By courtesy of Steel & Coal).

phosphorus in the range 0.02-0.03%, the initial slag is drained off and a second slag is made with or without the addition of lime, soda, etc., and blown further for a few seconds. In Phoenix-lance (PL) process¹⁸, the Thomas converter is tilted to horizontal position after initial bottom blow, oxygen is injected for some time and subsequently raised vertically and reblown with air. Fig. 2.12¹⁹ shows a typical blow. (See also p. 295).

The metallurgical aspects of all these processes are dealt with separately in subsequent chapters.

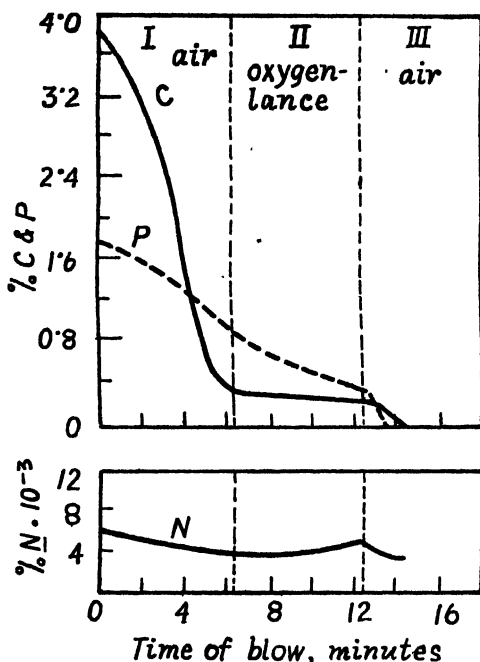


Fig. 2.12—Compositional changes of C, P & N during a PL blow.

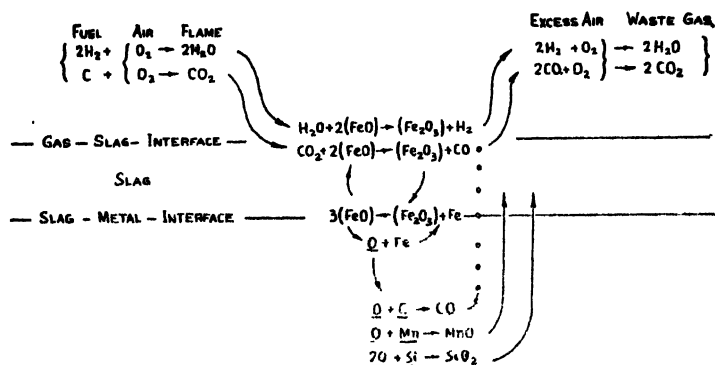
Open Hearth Processes

Although the steel made by the converter processes is naturally cheaper, the problem of producing quality steel of definite properties and specifications could not be fully solved. The reactions in pneumatic processes are so fast and since analysis of elements present in steel takes considerable time, it is difficult to maintain a proper control of the composition of steel. The pneumatic processes (except perhaps the newest oxygen lancing processes) require a pig iron of certain limiting composition which is difficult to obtain because of constantly varying types of iron ores and other blast furnace raw materials. Further, a large amount of scrap cannot be used in such processes because the heat evolved therein is self-generated by the exothermic oxidation reactions and is therefore limited.

Martin suggested the melting of pig iron and scrap in large open-hearth furnaces for the production of steel, the charge being heated to 1,600-1,650°C mainly by radiation of heat from the burning of gaseous fuels above it. It is not the amount of heat but rather the high temperature heat that is essential for the purpose. Such high temperature heat of temperatures around 2,000°C can be obtained by the burning of sufficiently pre-heated air and gas or of high calorific liquid fuels (with or without oxygen-enriched air). Such pre-heated air or gas is obtained by passing them through hot regenerators (a honey-comb of high-grade fireclay brick-works called *checkers*) which has been previously heated by the hot outgoing products of combustion from the furnace. This possibility of obtaining high temperature heat has led to the rapid universal use of open-hearth furnaces for the production of steel. Since the necessary heat for melting and refining of steel is supplied from outside, there is no limit for use of cold charges and even 100% scrap can be used. In practice, however, there is a fair proportion of molten pig-iron (or blown metal from bessemer) and scrap.

The oxidising media in open-hearth are the heating gases (products of combustion of gaseous and/or liquid fuels), carbon dioxide evolved from charged limestone (in basic process), iron or manganese (occasionally used) ores, scrap rust and scale. The burning of fuel reduces the oxygen-potential of the air and the combustion gases have average oxygen-pressure in the neighbourhood of 10^{-2} atm, although at some places it may be less where combustion has been incomplete or sluggish. At steel-making temperatures, the oxygen-pressure of liquid iron (as it is never saturated with oxygen) with normal carbon and oxygen is of the range 10^{-8} - 10^{-12} atm. Thus, there exists a considerable oxygen-pressure gradient from furnace atmosphere to the bath. There is a million-fold or more natural tendency for the oxygen of the heating gases to diffuse from high to low pressures and thereby oxidise the bath.²⁰ The intervening slag layer will probably have an oxygen pressure in-between the two, of the order of 10^{-4} - 10^{-11} atm. The probable mechanism of oxidation is that the heating gases convert the FeO in slag to Fe_2O_3 at the gas-slag interface, the latter migrating to slag-metal interface due to convection and reduced there to FeO according to $\text{Fe}_2\text{O}_3 + \text{Fe}$

→3 FeO. This FeO is partitioned between metal and slag and the equivalent oxygen in metal oxidises carbon and other foreign elements. The oxidising power of the slag is determined not by the amount or mol fraction of FeO in the slag but by its capacity for delivering oxygen to the metal (same as activity). The oxygen oxidises the carbon with the evolution of CO whose reducing and boiling action tend to maintain the slag layer less oxidising than normally possible. The oxidation mechanism can be seen from Fig. 2.13.²¹



[The solid lines under elements denote their presence in steel.]
Fig. 2.13—A schematic representation of oxidation process in open-hearth.
 (W.O. Philbrook & F.M. Washburn, Basic Open-hearth Steelmaking,
 AIME, Copyright 1951).

The evolution of CO from the carbon-oxygen reactions known as the *carbon boil*, creates a turbulence in the bath and is of extreme importance for open-hearth efficiency. It not only helps in the equalisation of concentrations of various components of the bath but what is more important, it also facilitates heat transfer from the heating gases to the metal. Carbon, as long as it is present in appreciable amount (more than about 0.05%), controls to a certain extent the oxygen potential of the bath. If the oxidation is, however, allowed to proceed to completion the whole of the bath will have reached an oxygen potential approximately that of the heating gases, i.e. 10^{-2} atm, which is about the same as that of Fe_3O_4 at steelmaking temperatures. Thus, if oxidation is not arrested at the proper moment the whole steel bath will be slowly converted to a product of composition approximating Fe_3O_4 with Fe_2O_3 , CaO, MnO, silicates, phos-

phates, etc., as impurities. It is, therefore, necessary to freeze up artificially the oxidation-reduction equilibrium of slag and metal, when the desired composition has been attained, by tapping the metal, or temporarily, by adding C, Mn to the metal bath or CaO, Al, Si to the slag.

The oxidised impurities are removed as slag (being almost insoluble in steel) except CO which is a gas and escapes. The slag is made acidic or basic according to the nature of foreign elements present in the bath. Phosphorus and sulphur can only be eliminated by basic slags. Lime is the commercial base used for the purpose.

Basic Open-hearth ²²

An open-hearth furnace consists of a hearth in the middle and roof at the top with flues for air and gas for heating on both sides. It can be either *stationary* or *tilting*. Tilting furnaces are used where the slag is to be removed or *flushed off* and a new slag made. The fuel used may be gas, liquid or a combination of both or sometimes together with solids such as powdered coke, etc.

The bottom and the banks are built-up with refractories that must not only hold steel at temperature of about 1,650°C but also withstand the attack of the slag which is highly reactive at such high temperatures. The bottom of the hearth is laid with several courses of insulating fire-clay and magnesite bricks with or without neutral chrome-magnesite bricks and finally the surface is produced by burning-in high-magnesia or tar-dolomite in successive layers.

The depth of the metal in hearth varies from 75cm to 125cm according to the charge used. If major portion of the charge is pig-iron, a greater amount of ore is used for oxidation. As ore prevents the passage of heat to the bath, a higher bath surface area per ton of metal is necessary for economical heating and the heat should therefore be performed in a shallow bath offering more surface. A shallow bath gives also more slag-metal and metal-hearth interface per ton of metal which are so important for the rate of carbon removal. High quality steel is generally made in shallow bath because at the end such a bath is less oxidised than deeper ones.

The open-hearth makes it possible to use scrap and pig-iron in all proportions, i.e. starting with 100% scrap to 100% pig-iron. The choice of the proportions depends upon the availability of the two. Bessemer blown metal having phosphorus and sulphur is also used and such a process is known as 'duplexing'. Initially the scrap and sometimes solid pig-iron together with limestone are charged into the furnace and fuel turned on fully. During this '*melt down*' period, considerable amount of iron is oxidised to FeO depending upon the exposed surface, light scrap being oxidised more than the heavy ones and the pig (as it contains carbon and silicon) is oxidised the least. The extent of this oxidation is important since, like ore, the oxidation products furnish oxygen for the elimination of metalloids later. Other elements present, such as C, Mn, Si and P (and also Al, Cr, V, Ti, etc. if they are present), may be oxidised during the melting period. Some of these oxides may be reduced later during the refining period depending upon their amounts and the amount and composition of the slag formed. Eventually, when the metal and the slag approach near equilibrium, these impurities distribute themselves between the metal and the slag (as their oxides) according to the chemical laws governing the heterogeneous system. There is generally, considerable sulphur pick-up from the heating gases during the melting period when the flame sweeps over the scrap directly and the extent of sulphur pick-up depends upon the length of this period and sulphur content of the fuels.

Depending upon the variations in steelmaking methods in different plants and countries, the molten pig iron may be added when the temperature of the furnace and the charge is high enough (so that the charge may not freeze up) and the scrap is partially melted. The oxidation of Si, Mn, P and C from pig-iron starts in the given order after the addition of molten iron, the source of oxygen being FeO formed from the scrap and the ore which is charged as the melting progresses. The oxidation of Si produces acid SiO_2 whereas that of Fe and Mn produce basic FeO and MnO. The initial slag formed, when lime has not or just partially come to solution, is composed of fusible acid iron-manganese silicates. The removal of phosphorus depends upon the available lime and also upon the activity of FeO in the slag, since dephosphorisation is facilitated by high basicity or CaO/SiO_2 or the so-called *V-ratio*

and high FeO content of the slag. Elimination of carbon starts when most of the silicon has been oxidised to silica.

The acid silicates are the major constituents of the slag before the start of the calcination of CaCO_3 which takes place when sufficient heat has gone down the bath (i.e. calcining temperature is reached). This usually happens before the completion of the above refining reactions. The calcination reaction $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ is endothermic and since also the limestone charged is in lump-form the evolution of CO_2 is slow. The evolution of CO_2 creates turbulence in the bath known as '*lime boil*' and thereby helps in the transfer of heat from the furnace atmosphere to the bath. It also supplements the oxygen required for the refining process since it is an oxidising agent, it itself being reduced to CO by the elements oxidised in the process.

The calcination produces CaO which is basic and reacts with the silicates to form calcium silicate and release FeO and MnO. As lime floats up to the slag, the latter changes its acidic character and its increase in basicity starts aiding phosphorus and sulphur removal. The liquid slag formed is a mixture of various constituents obtained during refining and from additions and refractories. They are generally silicates or double silicates of lime or other bases, ferrous and ferric oxides, manganese oxide and oxides of other impurities, phosphates of lime, alumina, magnesia, chromic oxide, etc.

The *working or refining period* starts when the melting is completed and most of CaCO_3 is calcined and rises to the top. The chief aims of this period are to attain a bath temperature suitable for *finishing* and tapping, the removal of most of the phosphorus according to specifications, and decarburisation at a speed commensurate with the rate of heat input and rising melting point of iron with decreasing carbon content and bring it down to a level to be dealt with during the finishing period. If too much of pig iron is used and/or too much Si and P are present in the charge the initial slag whose basicity should be between 1.5-2 is generally removed in order to decrease the slag bulk which would otherwise deteriorate the heat transfer to the bath and overheat the roof. In order to accelerate the oxidation of phosphorus, ore is sometimes used. After the removal of the initial slag lime, bauxite and/or fluorspar (CaF_2) are added to form a new slag. Generally, a

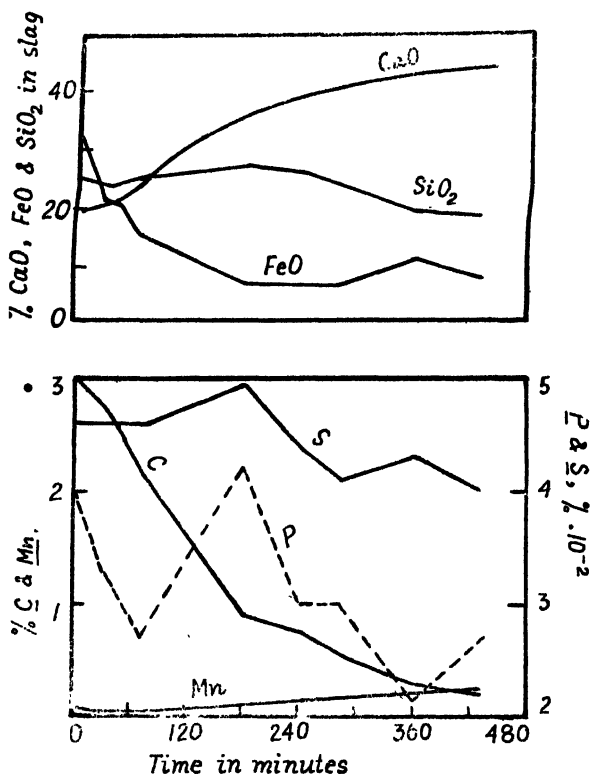
high rate of decarburisation is maintained during the dephosphorisation and the Mn-content maintained above 0.20-0.25%.

The lime coming to the top starts dissolving in the slag. After the 'melting' further oxidation is carried out by furnace gases acting indirectly through the slag. The 'carbon boil' is the only important reaction that continues upto the time of deoxidation and tapping. During the 'boil' a great care of the heat is taken by a systematic analysis of slag and the metal and by a close observation of the bath temperature and slag viscosity. If the slag is viscous, it is made thin by adding bauxite or CaF_2 . The basicity at the end of the heat is generally about 3.0. The charge is so calculated that the carbon-content at melt-down is about 0.4-0.5% higher than the desired specification. However, it is brought down a little below the desired level (for later adjustment in the furnace and the ladle) by suitably adjusting the slag during the boil in such a way as to have the other constituents within the prescribed specifications before tapping. The rate of decarburisation is controlled by additions of ore or lime. In a normal 'boil' the rate is 0.15-0.2% C/hr and after heavy oreing it is about 0.6-0.7% C/hr.

After the refining period only the final adjustments of temperature and composition of steel are made in what is known as the *finishing period*. The elimination of all the metalloids is virtually complete, phosphorus and sulphur are stabilised in the slag and decarburisation continues at a slow and steady rate before the finishing starts. There is generally, a slight manganese reversion to the bath which is a sign of proper bath temperature and slag composition and the state of oxidation. Final adjustments of composition are made with additions in the furnace or the ladle. The run of a basic open-hearth heat is shown in Fig. 2.14.

Acid Open-hearth

The open-hearth furnace and accessories are the same as in basic open-hearth. The hearth and the banks are made of acid silica bricks and rammed with quartzite with high SiO_2 and 3-5% bauxite as bond material. In view of the tendency of silica to spall due to volume changes with temperature, the maintenance of acid-hearth needs more care and attention than basic ones.



[The solid lines under elements denote their presence in steel.]

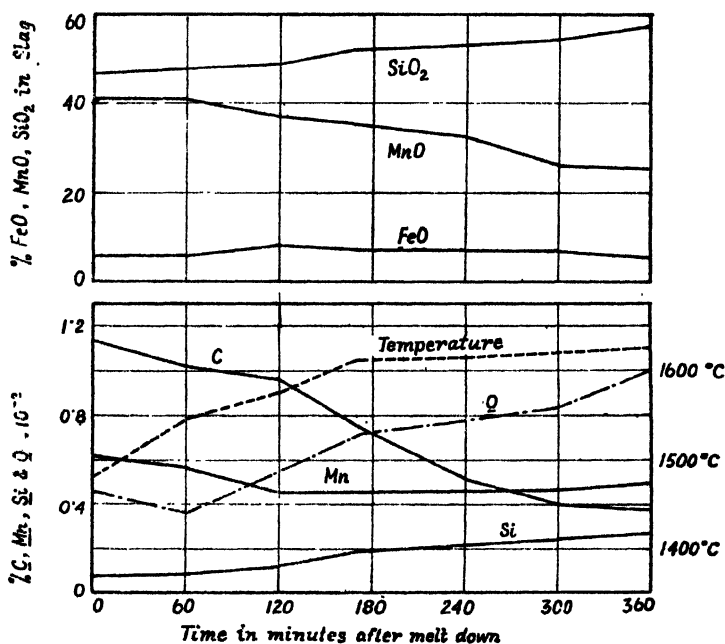
Fig. 2.14—A run of basic open-hearth heat.

With proper fettling with sand after every heat acid-hearths last for years.

The hearth surface becomes impregnated with iron oxides, MnO , Al_2O_3 , etc., during the course of the furnace operation. It is necessary to remove the surface layer by melting with sinter and lime and a new rammed layer made. This helps not only to increase the furnace life but is also essential for producing good quality steel. We will presently see, in the case of acid steels, unlike the basic ones, the hearth enters into reaction with the bath and the slag.

The pig iron used for acid open-hearth may contain low or high manganese. For low manganese the range is 0.3-0.5% whereas for high it may be 1.5-3.0%. S and P should be below 0.025-0.03%.

In acid open-hearth, fluxes are not used (except sometimes CaO and Al_2O_3) and, therefore, frequently the bath is not completely covered by slag. The slag itself is formed from oxidation products of the pig and scrap, i.e. FeO , MnO and SiO_2 and also from silica dissolved from the hearth. In order to cover the bath, sand and acid slag are to be added; otherwise the oxidation process will be accelerated by the direct impingement of flame without corresponding rise of temperature, with all the consequent troubles of cold heats. The run of an acid open-hearth heat is shown in Fig. 2.15.



[The solid lines under elements denote their presence in steel.]

Fig. 2.15—A run of acid open-hearth heat.

The acid open-hearth steel may contain both high and low silicon contents according to desire by proper control of the slag. The process can, therefore, be broadly divided into (i) 'passive' process where large amount of silicon is reduced to the bath, (ii) 'active' process where Si is reduced only to a limited extent.

(i) *Passive process* : The silicon reduction is caused by higher temperature (since $\text{SiO}_2 \rightarrow \text{Si} + 2\text{O}$ is endothermic) and by weakly oxidising slag saturated with silica and containing solid silica which makes the slag very viscous (see Fig. 3.19a). The viscosity depends on the content of SiO_2 , a slag containing 50-54% SiO_2 is reasonably fluid but with 55-65% is very viscous, which restricts the transfer of oxygen to the bath. The reaction of carbon with oxygen takes place at the hearth (*cf.* p. 188) which coupled with the inadequate supply of oxygen from slag causes carbon (as well as Mn and Fe) to react with SiO_2 of the hearth and reduce it to [Si]. The reduced Si reacts with the slowly diffusing oxygen of the slag at or near the metal|slag interface and is oxidised to SiO_2 which is incorporated in the slag thereby increasing its viscosity. Thus, there is a constant transfer of Si from hearth to slag.

The heterogeneity of the slag causes the Mn content of metal also to increase to values higher than the equilibrium content.

The oxidising capacity of the slag depends not only on the activity of (FeO) but also on the consistency of the slag. The latter alters according to silica-content. Thus, the reactivity of the slag can be controlled by addition of sand, fire-clay, etc. The Si-metal increases almost simultaneously with the increase of SiO_2 in slag. The Si reduction will be less, the more the slag is made fluid and oxidising by additions of iron ore.

(ii) *Active process* : In order to prevent an excessive Si-reduction, it is necessary, in view of what has been said in the preceding section, to increase the oxidising capacity of the slag by additions of iron ore (which increase the fluidity as well as the (FeO)-activity of the slag), prevent a large increase in temperature with the help of other coolants and add only limited amounts of lime (less than 10%).

Lime increases the solubility of SiO_2 in FeO-MnO- SiO_2 slags from about 50-54% without lime to about 65-70% with 10% lime. It also increases the fluidity as well as the oxidising capacity of the slag by reacting with iron silicates to liberate (FeO) and forming calcium silicate. The released (FeO) can restrict Si-reduction as well as oxidise [Si], thus keeping Si-reduction under control. Alumina increases the slag fluidity and behaves similarly as lime except that it is neutral to silicates.

The extent of decarburisation and Si- and Mn-reductions are controlled by proper adjustment of temperature and slag, by increasing or decreasing the slag fluidity with additions of ore, lime alumina on the one hand, and sand, fireclay on the other. Ultimate oxygen content of steel is much less than in basic open-hearth and thereby leads to better quality steel.

*Modern American Practice*²³

In America nowadays the refining of steel in acid open-hearth does not make it necessary to use ore or other oxidising additions. The rate of carbon removal is mainly controlled by increasing or cutting-back the fuel (i.e. by increasing or decreasing the temperature), thus enabling the *end or tapping carbon* to be approached at fast or slow rates according to desire. Moreover, the heat can be brought to the tapping temperature simultaneously with the attainment of the carbon specification. During the course of the reactions, for low manganese charge and therefore low MnO in slag which is generally about 12-15%, MnO remains practically constant whereas FeO decreases supplying oxygen for the carbon reaction. The Mn- and Si contents in the bath increase only slightly. On the other hand, if MnO exceeds about 30%, it is this oxide which suffers reduction and its percentage in slag decreases, whereas that of FeO is fairly level. It is apparent, in such cases, that MnO supplies the oxygen instead of FeO for the carbon reaction. The bath increases in Mn. In the intermediate range slags, i.e. in the neighbourhood of 25% MnO both FeO and MnO supply the oxygen, the percentages of both in the slag decrease to a certain extent and both the elements pass on to the bath. The silica content of slag, however, in all cases, increases and attains saturation. This automatic refining of steel in acid open-hearth has been explained by Fitterer²³ with the help of ionic theory of slags (*cf.* p. 175).

Electric Process

The principles involved in electric steelmaking are similar to those in open-hearth processes. In the latter processes the furnace atmosphere and therefore the slag have necessarily to be oxidising. In case of electric furnaces, the heating is performed (i) mainly by radiation as in the arc process where intense heat is produced by striking an arc between two or three graphite

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electrodes at very high KVA, or (ii) by induction where high or low-frequency currents are passed through water-cooled copper tubes wound round refractory-lined crucible-like vessels; in this process an eddy current stirs the metal and the turbulence thus created helps in slag-metal reactions. Since these furnaces can be closed with lids, air can have little access inside them and, therefore, a reducing (or oxidising) slag can be easily maintained according to desire. Owing to the high cost of electrical energy, only high grade and alloy steels are usually produced in such furnaces. The refractory lining may be acid or basic as in open-hearths.

In basic process, the charge usually consists of scrap, lime and a carburiser. The refining is carried out in two stages (i) with *oxidising slag* and (ii) with a *reducing slag*. During the oxidising period the charge is fed, after the melt down, with ore, oxygen gas through lance, fluorspar, lime according to the prevailing rate of decarburisation and silicon-and phosphorus-contents of the charge. With oxygen lancing the bath gets rapidly heated to 1,700-1,800°C and carbon removal increases greatly; it is very useful, specially when carbon level is low and decarburisation sluggish. Although a little of sulphur is also eliminated, the primary purpose of the oxidising period is (i) oxidation and removal of mainly silicon and phosphorus, (ii) maintenance of sufficient carbon boil for the removal of hydrogen, good slag-metal contact, good heat transfer (in arc furnace). This oxidising slag is rather black in colour because of the presence of FeO. It is almost completely removed before the next stage begins.

After draining off the first or oxidising slag, the charge is fed with lime, fluorspar, coke and some sand for making the reducing slag. At the high temperature already reached at the end of oxidation refining, the carbon reacts with lime and forms calcium carbide :



However, the carbide formed is destroyed immediately by (FeO) -slag :



This reaction continues as long as any oxygen is left in the metal since it continually diffuses out to the slag which, having been

denuded of oxygen by the carbide, is at a lower oxygen potential. When oxygen transfer is almost complete, the carbide becomes stable and the slag assumes a greyish color. The carbide slag, known as *white slag*, can be easily recognised from the typical carbide smell when damped with water. Sulphur is extensively removed by such a slag :



The disadvantage of the carbide slag is that it leads to carbon pick-up by the metal. For producing *soft* steels (low carbon), generally ferro-silicon or ferro-aluminium are added for obtaining the reducing slag. They cause extensive reduction of Mn, Cr and other alloying elements from slag to metal. The alloying elements, mostly as ferro-alloys, are added during the reducing period.

The advantages of electric steels are their low sulphur, phosphorus and oxygen contents. The amount of inclusions is much less than in other processes because deoxidation takes place in the furnace itself by 'diffusion' and not by 'precipitation' with the help of deoxidisers which results in the formation of insoluble oxides.

The acid process has limited applicability since only scrap with low phosphorus and sulphur can be used. The lining is made of silica bricks. The scrap may be melted without additions of slag and sand. Ore addition is not necessary before the carbon boil starts if the melt down slag is fluid and dark. Manganese and silicon undergo the usual oxidation reactions. The vigour of the boil is maintained according to desire by feeding of ore until the melt attains the specification.

Deoxidation

The making of steel is an oxidation process. Therefore, some *residual oxygen* is always left in the metal after the refining is over. Since the solubility of oxygen decreases with falling temperature, it would separate out (as FeO), i.e. undergo an automatic deoxidation when the metal solidifies. If this oxygen is not kept under proper control, it leads to internal and external defects and affects the hot workability and castability of the metal.

The ingots may crack or break during rolling or forging (*red shortness*).

The oxygen is removed or kept under control by deoxidisers like Mn, Si, Al, Ti, Zr, which possess very great affinities for oxygen. The last three are generally added in the ladle whereas the first two in the form of ferro-alloys can be added in the furnace shortly before tap or in the ladle. The deoxidisers form insoluble oxides which should separate out. They cause, when present, inferior ductility, workability, mechanical strength, grain-size as well as strain-ageing. When most of the oxygen is removed we get *killed* steel; with insufficient removal we get *semi-killed* and *rimming* varieties. These are discussed in the following section.

Ingot making

The liquid steel is poured or *teemed* from the teeming ladle from the top or from the bottom through refractory runners into cast iron moulds where it solidifies and is then taken out for subsequent rolling or forging.

As soon as a fully killed liquid metal comes in contact with the cold walls of the mould a thin skin or *chill* of fine-grained crystals is immediately formed having the same composition as the metal. Thereafter a new set of *columnar* crystals begins to grow towards the centre perpendicular to the mould wall and offshoots from these crystals at right angles give a *dendritic* formation. When the crystallisation has proceeded so far as to be out of the influence of the mould wall, the large numbers of nuclei present begin to grow freely and form *equi-axed* crystals. Due to the contraction of the metal during cooling, shrinkage cavities known as *pipes* occur. For steel containing upto 1% carbon, the extent of shrinkage is about 11%. The pipes generally occur in the upper portions of the ingots since any shrinkage cavity in the lower portions is fed by gravity from the mother liquor or the *rest metallic melt* of the solidifying metal. The upper portion is generally sheared off as the pipes do not weld up during subsequent mechanical treatment because of aerial oxidation of the cavity surface.

According to the laws of crystallisation, the impurities present in the metal should separate out as solidification proceeds and pro-

gressively concentrate in the rest metallic melt causing extensive *segregation* of C, Mn, S, P and others. It does not, however, occur in killed ingots to any great extent. The impure melts adjacent to the metal crystals are entrapped in the dendritic network and solidify there without causing any excessive concentration of the impurities in the liquid portion. The picture, however, changes in the case of semi-killed or rimming varieties where carbon-oxygen reaction causes evolution of CO gas. The consequent boil or *effervescence* disturbs the crystallisation process and displaces the entrapped impure liquid from the dendritic network. The displaced liquid joins the main liquid metallic pool which becomes progressively impure and enriched with the metalloids resulting in widespread segregation in the central zone.

The freezing conditions, as narrated in the case of killed steel, change substantially in the case of semi-killed and rimming varieties where oxygen is only insufficiently removed. The carbon and oxygen react when equilibrium concentrations are attained during freezing for the evolution of CO gas against the atmospheric and hydrostatic (ingot head) pressures. The gas evolution not only disturbs the crystal formation but some of the bubbles may fail to escape and form the so-called *blow-holes*. The number and position of the blow-holes in rimming ingots depend upon the carbon, manganese and oxygen contents since silicon is almost absent (*cf.* p. 392). Blow-holes near the surface are not desirable since they open up during the rolling and cause surface defects. This generally happens when the C-O reaction is sluggish and CO gas is entrapped in the extending crystal network. A good and thick solid rim is obtained if the gas evolution is strong enough to wash away any initial entrapped bubbles resulting in the desired deep-seated blow-holes. Pipes are more or less absent in rimming steel as the shrinkage volume is balanced by the total volume of the blow-holes. The blow-holes are less numerous in semi-killed ingots and, therefore, small pipes may occur. Apart from CO, the blow-holes contain hydrogen as well which probably diffuses from the surrounding metal, when its solubility decreases as the metal freezes, into the gas pockets formed from CO.

Rimming and semi-killed steel give good surface characteristics but show considerable segregation, more so in the former. How-

ever, there is less waste in discards than in the killed variety. The yield in semi-killed variety is the largest and therefore maximum tonnage is made from this type. Rimming steel is generally used for flat products because it gives very good surface. The killed variety is good for casting and forging purposes.

Ingot making is a subject by itself. Only a brief outline has been given here for its relation with the retention of CO in steel discussed in Chapter 12. For a detailed study and bibliography, the reader may refer to other sources.²⁶

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CHAPTER III

SYSTEMS OF IMPORTANCE IN STEELMAKING

Fe

IRON occurs in two allotropic forms viz : α —and δ —having body-centred cubic and γ —face-centred cubic lattice. α —iron is stable upto 906°C when it is transformed into the γ —form. γ — δ transformation occurs at 1401°C . δ — form exists upto the melting point of iron ($1,535^{\circ}\text{C}$). There is another change of α — iron at about 720°C (sometimes called β — transformation) when iron loses its ferro-magnetism. This is known as *Curie point*.

Pure iron is not useful for most of the purposes. For imparting technological properties, it is necessary to alloy the metal with different elements like C, Mn, Si, Cr, Ni, Mo, V, etc.

Some elements viz : C, Mn, Ni enlarge the γ —field and some narrow it down viz : Si, Cr, Mo, etc.

Fe—O

Steel is obtained from pig iron by the oxidation and removal of the impurities. Oxygen remaining in the bath or transferred from slag plays an important part as regards the quality of the finished steel. It is important to know the behaviour of oxygen with regard to liquid iron whether in open-hearth or in converters or in any other steelmaking process, since the rate and method of supply of oxygen decide the overall rate of the processes and the final or residual content of oxygen in the steel bath. The amount of inclusions in steel is intimately connected with the residual oxygen (which is primarily responsible for the appearance of oxide inclusions). These inclusions deteriorate the quality of the steel. It is the prime motive of any steel technologist to have as little oxygen as possible in steel after the refining period (under, however, certain conditions described in Chapter 10). However, if a 'boil' or 'rim' is necessary in ingots, a certain minimum amount of oxygen is absolutely necessary.

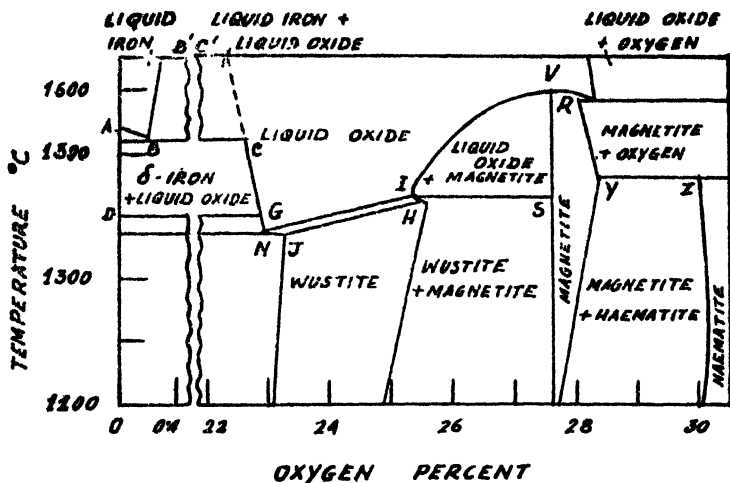
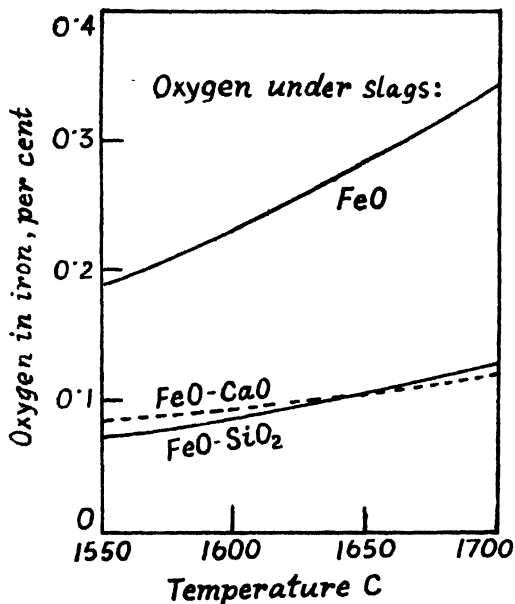


Fig. 3.1—A section of the Fe-O phase system.

Fig. 3.2—Oxygen solubility in liquid iron at various temperatures under pure FeO, lime saturated FeO-CaO and silica saturated FeO-SiO₂ slags.

The form in which oxygen is present in iron is not fully proved but for our purposes it may be taken for granted that it is present

as $[\text{FeO}]$ or $[\text{O}]$ and not as any other oxide. Considering from what has been said, it is evident that for the purpose of steel production we are concerned with that part of Fe-O phase diagram which deals with liquid iron under steelmaking temperatures. In Fe-O phase diagram, Fig. 3.1¹, the line starting at B has a special significance since it gives the solubility of oxygen in iron as a function of temperature in presence of liquid FeO slag. Pure iron melts at $1,535^{\circ}\text{C}$ (point A in Fig. 3.1) and with increasing oxygen-content the m.p. decreases along the liquidus line AB until the point B is reached corresponding to $1,524^{\circ}\text{C}$ and $0.16\% \text{—}[\text{O}]$. If the supply of oxygen is maintained and the temperature is increased, the liquid iron takes up more and more oxygen and follows the line BB' which is same in sense as the oxygen-solubility curve of Feters and Chipman,² and Taylor and Chipman³ (Fig. 3.2). At $1,600^{\circ}\text{C}$ the solubility is about 0.23% and at $1,700^{\circ}\text{C}$ about 0.3% . Thus, if a sample of pure liquid iron at $1,600^{\circ}\text{C}$ is treated with air or oxygen, it would take up oxygen until the saturation value of $\sim 0.23\%$ is reached. Above this saturation value further treatment with oxygen will lead to a separate phase of liquid FeO which, because of the presence of a miscibility gap, separates out in another layer and being lighter lies above the liquid iron. As long as liquid metallic iron exists as a second phase in equilibrium, oxygen will be present as FeO and not as any other oxide. Only when the entire metallic iron is converted to FeO, further oxidation will lead to higher iron oxides. At steelmaking temperatures, i.e. in the neighbourhood of m.p. of iron, only Fe_3O_4 can possibly exist as higher oxide since Fe_2O_3 is unstable at these temperatures. The m.p. of the oxide slag increases as more and more of Fe_3O_4 is formed and taken up in solution, as can be clearly seen in Fig. 3.1.

The above becomes clearer from the consideration of Fig 3.3 (a)⁶ & (b). Fig. (a) depicts the relationship between the oxygen pressures of various phases of the iron-oxygen system at different temperatures. These can be obtained from the free energy equations of different iron oxides at different temperatures, e.g.



$$\Delta G^{\circ} = RT \ln p_2\text{O} = -119,250 + 67.25 T \quad 3.1$$

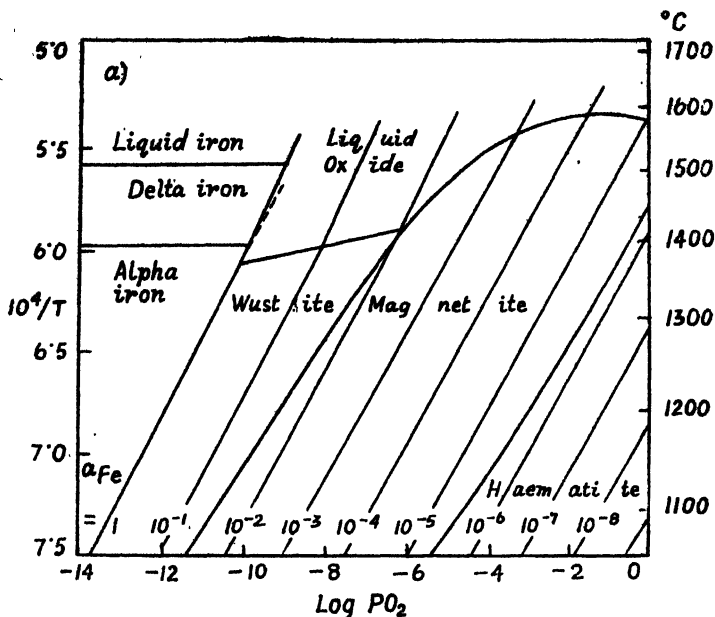


Fig. 3.3—(a) Oxygen pressure of iron oxides and oxygen dissolved in iron at various temperatures. Activity of iron is also shown.^a

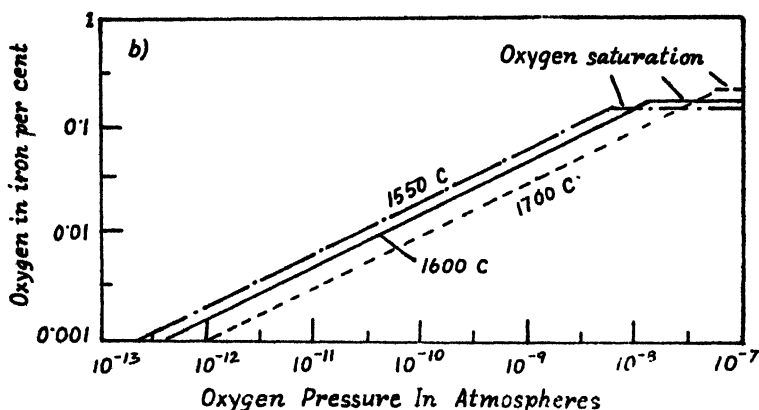


Fig. 3.3—(b) Amount of oxygen dissolved in liquid iron at various temperatures and pressures of oxygen (calculated),

from where p_{O_2} at any temperature can be calculated. Fig. (b) shows the p_{O_2} in equilibrium with varying amounts of oxygen in liquid iron at 1,550°, 1,600° and 1,650°C. These again can be calculated from the free energy of dissolution of oxygen in iron. According to Dastur and Chipman,⁷

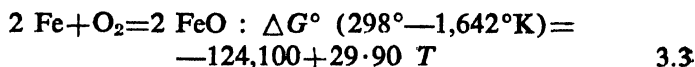
$$1/2 O_2 = \%[O] : \Delta G^\circ = -27,930 - 0.57 T \quad 3.2$$

$$K = \%[O] / p_{O_2}^{1/2}$$

$$\log K = -\Delta G^\circ / RT = 6,100/T + 0.125$$

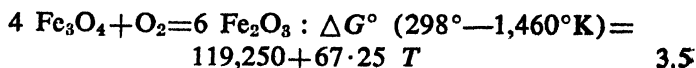
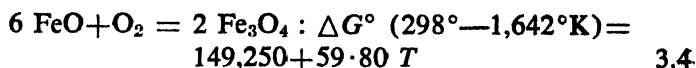
from where p_{O_2} at different % [O] at various temperatures can be calculated. In this figure the solubility limits are also shown. It is clear from here that any atmosphere having oxygen pressure of more than about 10^{-8} atm would be oxidising to iron and ultimately saturate it with the formation of oxide. Fig. (a) shows the different phases which would ultimately be reached in such an oxidising atmosphere. At 1,550°C an oxygen pressure of more than about 10^{-9} atm. would convert oxygen-saturated liquid iron completely into liquid iron oxide; whereas, if oxygen pressure is in excess of about 10^{-4} atm., solid magnetite (Fe_3O_4) will be formed.

The free energies of formation of various iron oxides are given below : ⁸



$$\Delta G^\circ (1,642^\circ - 1,808^\circ K) = -103,950 + 17.71 T$$

$$\Delta G^\circ (1,808^\circ - 2,000^\circ K) = -111,250 + 21.67 T$$



The oxygen-pressures at steelmaking temperatures are : ⁴

	PO ₂ in atm. at °C			
	1500	1550	1600	1650
2 FeO(l) = 2 Fe(l) + O ₂	1.07.10 ⁻⁹	2.46.10 ⁻⁹	5.46.10 ⁻⁹	1.2.10 ⁻⁸
2 Fe ₃ O ₄ = 6 FeO(s) + O ₂	4.68.10 ⁻⁸	1.48.10 ⁻⁸	4.46.10 ⁻⁸	1.23.10 ⁻⁸
6 Fe ₃ O ₄ = 4 Fe ₂ O ₃ + O ₂	1.0	1.5	6.05	13.8

The experimental work for finding the solubility of oxygen in iron was undertaken by Hertzy⁹ and Körber & Oelsen.¹⁰ They used MgO crucible for the melt and the results are not reliable since MgO reacts with FeO. Taylor and Chipman⁸ have used rotating crucibles where FeO-slag is not allowed to come in contact with the vessel. They give the following solubility equation :

$$\log [\text{O}]_{\text{max}} = -6,320/T + 2.734 \quad 3.6$$

The maximum solubility of oxygen in iron is exhibited when it is in equilibrium with a slag of pure FeO at any given temperature. If the slag is diluted by other oxides the amount of dissolved oxygen would vary. It will be proportional to the mol fraction of FeO if the latter behaves ideally in the slag system. Since oxygen in iron is delivered only by (FeO)-slag the Nernst distribution law will hold good and will take the following form :

$$L_{\text{FeO}} = (\text{FeO}) / [\text{O}] \quad 3.7$$

where (FeO) is calculated in mol fraction from the total iron content of slag and [O] is the oxygen in metal as found from analysis. L_{FeO} is a constant for all slags provided (FeO) behaves ideally and is only dependent upon the temperature. Körber and Oelsen¹¹ give the value of L_{FeO} as 4.75 at 1,600°C for iron melt under acid slag (FeO-MnO-SiO₂). This has been further dealt with on p. 153. Schenck¹⁵ recommends the use of the constant provided FeO in slag is presumed to be present as 'free' or in an uncombined state (*cf.* chap. IV).

In slags where FeO does not behave ideally the distribution constant becomes variable. Liquid iron under a silica-saturated FeO-SiO₂ slag with about 50% FeO or 39% total iron dissolves 0.09% [O] at 1,530°C and 0.13% at 1,700°C. The temperature function of the solubility is given by :⁵

$$\log [O] = -6,120/T + 2.212 \quad 3.8$$

In case of basic slag, e.g. lime-saturated FeO-CaO system with 38% CaO the rest being di- and tri-valent iron with about 44% total iron, the O-contents of iron are almost the same as under the acid slag. The temperature function is given by⁴ :

$$\log [O] = -4,030/T + 1.13 \quad 3.9$$

It can be seen from Fig 3.2 that although the iron-contents are very different, the oxygen contents are almost identical. They are, however, much less than in case of melts under pure (FeO)-slag.

The amount of dissolved oxygen will vary, not in proportion to the mol. fraction of FeO but rather according to the iron oxide activity of the slag. Such an activity is the ratio of actual amount of oxygen in iron under the slag to that of maximum oxygen under pure FeO at the given temperature derived from Eq. 3.6. As for example, the maximum solubility at 1,600°C from Eq. 3.6 is 0.23%. If 0.115% of oxygen is found by analysis under a given slag, then the activity of FeO in slag is :

$$a_{\text{FeO}} = 0.115/0.23 = 0.5 \quad 3.9a$$

For pure FeO, the activity is naturally unity. Such activity curves of slags are given at various places in the book. In fact, iron oxide activity corresponds to oxygen pressure but the former is more convenient to use. Conversion of the activity into oxygen pressure is simple :

$$\begin{aligned} p_{\text{O}_2} [O] &= a_{\text{FeO}} \cdot p_{\text{O}_2} (\text{pure FeO}) \\ p_{\text{O}_2} \text{ for FeO at } 1,600^\circ\text{C} &= 5.46 \cdot 10^{-9} \\ \therefore p_{\text{O}_2} [O] &= 0.5 \cdot 5.46 \cdot 10^{-9} = 2.73 \cdot 10^{-9} \end{aligned}$$

Oxygen dissolved in steel behaves ideally upto the saturation limit. It obeys Henry's law and therefore oxygen activity term in any equilibrium reaction can be replaced by weight per cent of dissolved oxygen. Recently, however, it has been reported that there is a slight variation of the activity coefficient of oxygen with concentration (cf. p. 127).

Fe—C—O

The solubility of oxygen in liquid iron given in the preceding section concerns only the pure Fe—O system. In the presence of a slight amount of carbon of the order of 0.01% or so, the system becomes unstable and oxidation of carbon starts forming CO and CO₂. The reaction will continue until either carbon is completely oxidised away by the FeO-slag in which case the system will follow thereafter as in previous section or the entire FeO-slag will disappear leaving an atmosphere of CO and CO₂ in equilibrium. The following are the possible equilibria :

$$(a)^{12} [C] + [O] = CO(g) : \Delta G^\circ = -8,510 - 7.52 T \quad 3.10$$

$$\log K = \log P_{CO} / (\% [C] \cdot \% [O]) = 1,860/T + 1.643$$

Usually the equation is referred to as, $\% [C] \cdot \% [O] = m \cdot p_{CO}$ 3.10a

At $p_{CO} = 1$ atm and at 1,600°C, $m = 0.0025$

$$(b)^{12} [O] + CO = CO_2 : \Delta G^\circ = -38,050 + 20.72 T \quad 3.11$$

$$\log K = \log P_{CO_2} / ([O] \cdot p_{CO}) = 8,316/T - 4.53$$

$$(c)^{18} [C] + CO_2 = 2CO : \Delta G^\circ = 33,300 - 30.40 T \quad 3.12$$

$$\log K = \log P_{CO}^2 / ([C] \cdot P_{CO_2}) = -7,280/T + 6.65$$

In steelmaking, the reaction of carbon and oxygen takes place in the bath and therefore follows equation (a) which is a function of CO-pressure only. The partial pressure of CO₂ under steel-making conditions is small and constant. One may therefore neglect equations (b) and (c) so far as decarburisation of steel

bath is concerned. The percentages of CO_2 in the equilibrium gas at one atmosphere at $1,600^\circ$ and $1,650^\circ\text{C}$ are given in Table 3.1.¹²

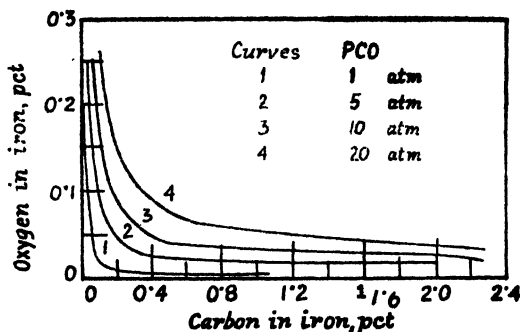


Fig. 3.4—Carbon & oxygen equilibrium relations at high pressures at $1,600^\circ\text{C}$ (J. Chipman, Basic Openhearth Steel-making, AIME, Copyright 1951).

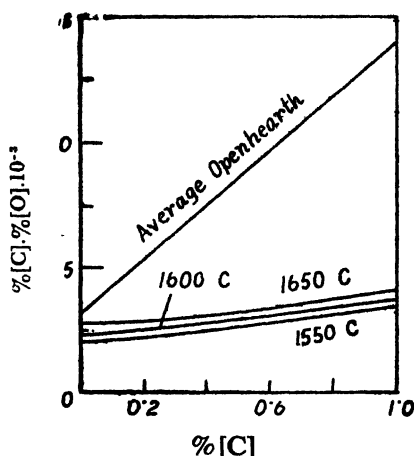


Fig. 3.5—Variations of $m = \%[\text{C}]\%[\text{O}]$ with $[\text{C}]$ in the laboratory at different temperatures as well as in the openhearth.

The C-O equilibrium has been the subject of numerous investigations.^{13,14,22} The value of Vacher and Hamilton,¹⁴ $[\text{C}]\cdot[\text{O}] = 0.0025$ at $p_{\text{CO}} = 1$ atm and $1,600^\circ\text{C}$ is accepted by most as applicable to steelmaking. Schenck *et al*¹⁵ and Marshall and Chipman¹⁷ suggest that the product of C and O is not a constant and increases with increase of carbon. There is also a slight but

not negligible temperature-function of the product. The change in the activity co-efficients of [C] and [O] and in the values of % [C].% [O] at 1 atm of $\text{CO} + \text{CO}_2$ for 1,600° and 1,650°C are given in Table 3.1. Since the equilibrium product is again a function of p_{CO} -pressure, the product will increase or decrease according as p_{CO} is above or below 1 atm. Fig. 3.4 shows the influence of high pressures on the equilibrium as found by Marshall and Chipman in their laboratory experiments.

TABLE—3.1¹³

%C	f_{O}	f_{C}	% [C]. % [O].10 ^a CO + CO ₂ = 1 atm		%CO ₂ in equilibrium gas = 1 atm	
			1,600°C	1,650°C	1,600°C	1,650°C
0.01	1.00	1.00	1.98	2.16	14.0	11.9
0.02	0.99	1.00	2.12	2.29	8.0	6.7
0.05	0.97	1.00	2.29	2.45	3.5	2.9
0.10	0.94	1.01	2.38	2.54	1.8	1.5
0.20	0.88	1.03	2.50	2.67	0.9	0.7
0.50	0.74	1.10	2.81	3.05		
1.00	0.55	1.23	3.40	3.63		
2.00	0.30	1.70	4.50	4.80		

Eq. (a) above when converted into wt. % takes the following form :²²

$$\log (\% [\text{C}]. \% [\text{O}]) / p_{\text{CO}} = \log K_a + 0.22 \% [\text{C}] + 0.315 \% [\text{O}] \quad 3.13$$

According to Elliott,²² the equilibrium oxygen increases greatly above about 2% C, as shown in Fig. 8.14. Fig. 3.5 obtained from the same equation shows the variations of $m = \% [\text{C}]. \% [\text{O}]$ with carbon at 4 different temperatures.²² This figure also includes m in open-hearth practice.

The equilibrium curve of Vacher and Hamilton and also other such curves at various pressures are drawn in Fig. 3.6. The curves for $p_{\text{CO}} = 1.1$ atm or $p_{\text{CO}} = 0.45$ atm are of special significance since according to Schenck²³ they are the pressures at

which carbon monoxide is evolved from the steel bath with slag cover (ferro-static pressure) under normal operation of open-hearth and bottom-blown converter processes. In the latter process the p_{CO} is low because of dilution by the aerial nitrogen.

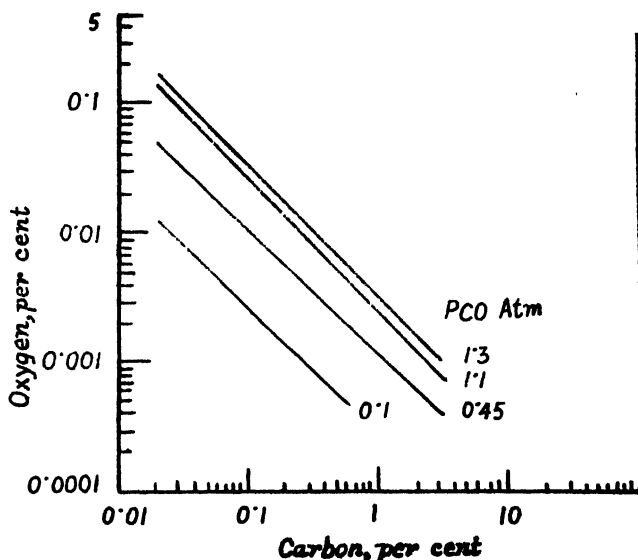


Fig. 3.6—Carbon-oxygen equilibrium relations at low pressures and at 1,600°C.

From Eq. 3.10a it is clear that the solubility of oxygen in iron is greatly lowered in the presence of carbon, e.g. at 1,600°C, the oxygen solubility is 0.05% at 0.05% C, 0.025% at 0.1% C, 0.01% at 0.25% C and 0.005% at 0.5% C and so on. These may be compared with 0.23% [O] at 1,600°C in carbon-free melts. The oxygen will be less, as mentioned before, where p_{CO} is less than 1 atm. e.g. in converter or when subjected to vacuum. If oxygen in pure form or in mixture, as in air, is brought to react with an iron-carbon alloy, the oxygen will react until equilibrium with [C] is reached which is dependent on the partial pressure of CO in or over the bath. Therefore it is not the same if pure or mixed oxygen is used, or the bath depth is high or low. Of course, the reaction $[C] + O_2 = CO_2$ must be taken into account and it is possible that such a reaction affects certain carbon-oxygen calculations (see p. 212).

As regards the ferro-static pressure in steel bath, as mentioned before, Schenck²³ has calculated that in a bath of depth 0.6—0.75 m and slag layer of 0.3—0.4 m, such a pressure is about 1.3 atm. Further calculations, taking CO_2 into account, gives $p_{\text{CO}} = 1.1$ atm. in open-hearth. In case of bottom blown converters, assuming that aerial oxygen is completely transformed to CO, although the total gas pressure is 1.3 atm. yet p_{CO} is maximum of about 0.45 atm. From Fig. 3.6, for C—O equilibrium curve at 0.45 atm, the oxygen content of liquid iron is about 0.002% at 0.5—0.6% C or above. The C—O equilibrium above 0.4% C, however, behaves abnormally in steel bath. At higher carbon contents the product m gives higher values. An increasing temperature also gives higher values. In both the latter cases, the oxygen-content will increase for a given carbon-content (Fig. 3.5).

Fig. 3.32 serves as a theoretical basis for deoxidation of steel under vacuum and without the use of metallic deoxidisers. Steel containing 0.1% C at 1 atm. and 1,600°C would have an equilibrium oxygen content of 0.025%. At the same C-content and at 0.01 atm. equilibrium pressure, the new oxygen level would be 0.00025, which is about 100 times less. If a potent deoxidiser like aluminium is used, 0.1% Al would be in equilibrium with 0.0025% [O], which is only 10 times less. Although vacuum deoxidation by carbon is superior theoretically, it is handicapped by the almost prohibitive cost of such a process and also by the fact that since the product of deoxidation is a gas (CO) the nucleation of CO bubbles may be inhibited. The forces of surface tension of steel and capillary over-pressure, etc. come into play (see p. 188).

It is clear from Fig. 3.6 that at any temperature, as the oxidation of carbon proceeds, the oxygen-content increases as carbon falls. As for example, at 1,600°C during oxidation by air ($p_{\text{CO}} = 0.45$ atm.), the oxygen content is 0.005% at about 0.20% C and 0.01% at about 0.10% C. Oxidation by pure oxygen or for pure C—O reaction as in open-hearth where $p_{\text{CO}} = 1.3$ atm., the values are 0.005% for 0.65% C and 0.01% for 0.32% C. In case of open-hearth, as we will see later, the rate of decarburisation and the metal oxygen are inter-related. As the oxygen supply increases, the rate of decarburisation also increases. For a given carbon content the oxygen content increases in a sense

proportional to decarburisation rate which is equivalent to CO evolution under increased pressure. According to Oelsen, CO-evolution is a physical process and depends on the facilities available for bubble-formation which should decide the reaction rate. This postulation has led to a great controversy. The subject has been handled in detail in Chapter 5.

Steel is made in furnaces or vessels with refractory linings. These refractories contain highly stable oxides like Al_2O_3 , SiO_2 , MgO , CaO , etc. Since the carbon in steel is in a dilute solution and since the oxygen dissociation pressures of these oxides are low even at very high temperatures, it is improbable that carbon will react with these refractory materials. But oxygen present in steel as FeO may be able to 'flux' these oxides. From Figs. 3.40 & 3.41, the phase diagrams of FeO and the above oxide systems, it is easy to find out the percentages of FeO that will form a liquidus with the oxides at steelmaking temperatures, e.g. at $1,700^\circ\text{C}$ 94% FeO will be necessary for the liquefaction of MgO . Since (FeO) -slag is related to oxygen-content of iron, it can be calculated how high should the $[\text{O}]$ -content be in order to furnish enough FeO in the slag for the liquefaction. From Eq. 3.6, $[\text{O}]$ (max) under pure FeO -slag can be found out from the temperature function. A rough estimate can be made of the amount of oxygen that must be present in iron in order to furnish a certain (FeO) -content of slag, by simple proportionality calculations. As for example, at $1,700^\circ\text{C}$, $[\text{O}]$ (max) = 0.28% for 100% (FeO) . For 94% (FeO) , $[\text{O}] = 0.28.94/100 = 0.26\%$. (Such estimations are extremely approximate and the results may vary widely from the actual, since, as we have already indicated, the oxygen in steel depends upon a_{FeO} and not on the amount of the slag oxide). For the presence of such a high oxygen in iron, the amount of dissolved carbon must be extremely small; such high iron-content of slag is never attained in practice. Carbon is a very strong reducing agent and it never allows such a high build-up of FeO in the slag as long as it is present in any significant amount.

Even under reduced pressures, e.g. in the converters, this is impossible. The same argument applies to other linings like SiO_2 , Al_2O_3 , etc. Fig. 3.7²⁴ gives the relation of $[\text{C}]$ and FeO in acid and basic slags. The increasing (FeO) -slag, in equilibrium

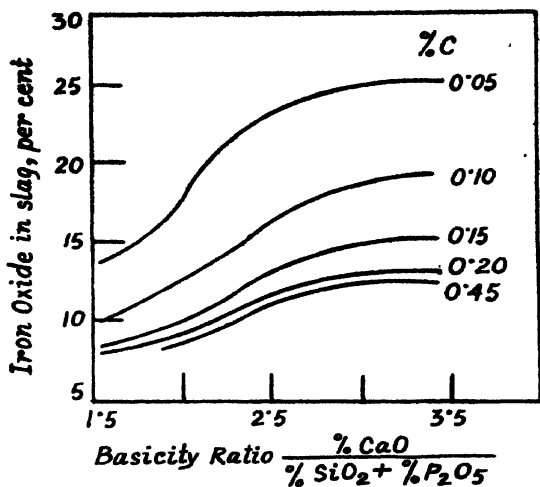


Fig. 3.7—Dependence of the amount of iron oxide in slag on basicity for various carbon contents of metal. (W. O. Philbrook & F. M. Washburn, Basic Openhearth Steelmaking, AIME, Copyright 1951)

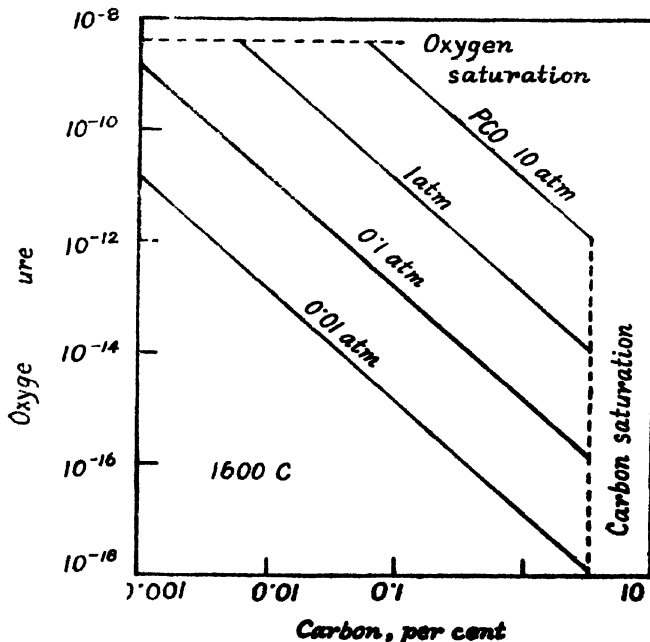


Fig. 3.8—Oxygen pressures in iron containing carbon at various partial pressures of CO.

with a given $[C]$, with increase in basicity is due to the fact that the a_{FeO} decreases above a lime-silica ratio of 2.7 (cf. Fig. 4.5).

It may not be irrelevant here to discuss the oxygen pressure in carbon-containing liquid iron and the CO_2/CO ratio in equilibrium with it. For CO_2/CO ratio the relevant equation is given by Eq. 3.12. The equation for oxygen pressure is²²

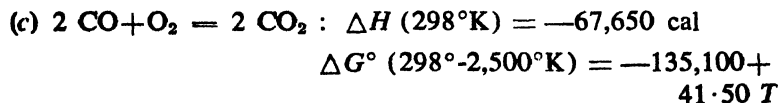
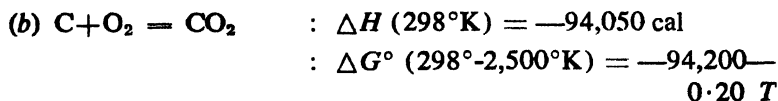
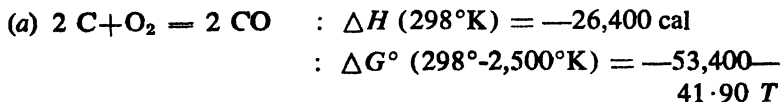
$$\begin{aligned} \%[C] + \frac{1}{2}O_2 = CO : \Delta G^\circ &= -33,500 - 10.15 T & 3.14 \\ K = p_{CO} / (\%[C] \cdot p_{\frac{1}{2}O_2}) : \log K &= 7,320/T + 2.22 \end{aligned}$$

The relation obtained from these equations are shown in Fig. 3.8 for various total pressures $CO + CO_2$ in atmospheres. Below the oxygen pressure $p_{O_2} \sim 10^{-9}$ the curves are as well valid for pressures of CO only since p_{CO_2} is negligible. Above the said oxygen pressure, p_{CO_2} starts being significant in the gas phase and as a consequence these curves shift slightly towards the left.

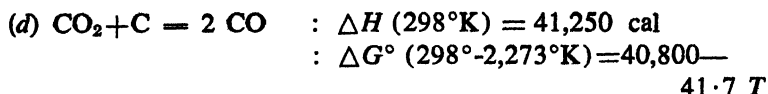
It is interesting to note the great reduction of oxygen potential from oxygen saturation to 2% C at $1,600^\circ C$. The oxygen pressure decreases about 10^5 times as can be seen from the figure.

$C-O^{2s}$

There can be four possible reactions in this system :



$$\log K_c = \log p^2_{CO_2} / (p^2_{CO} \cdot p_{O_2}) = 29,500/T - 9.1$$



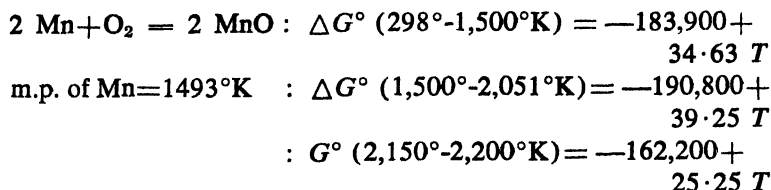
when excess of carbon is present, its activity may be assumed to be constant. The reaction is also a function of pressure. If the total pressure is P and x mol. fraction of CO is formed, then

$$p_{\text{CO}_2} = P (1-x) \text{ and } p_{\text{CO}}^2 = P^2 x^2$$

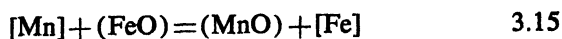
$$\text{Therefore, } K_d = p_{\text{CO}}^2 / (p_{\text{CO}_2} \cdot a_{\text{C}}) = P \cdot x^2 / (1-x)$$

$$\text{where } \log K_d = -8,920/T + 9.12$$

Fe—Mn—O



Manganese has always been thought by steelmakers as of importance for the steel quality. Since it is a costly metal its removal in the slag is also of importance. The oxidation of manganese in liquid iron may lead to FeO—MnO solid solution or FeO—MnO liquid slag. It is worthwhile to mention here that FeO & MnO are completely miscible in solid as well as liquid solution and they behave ideally in such solution (see Fig. 3.40a). The oxidation reaction can be written as



$$K_{\text{Mn}} = \% (\text{MnO}) / (\% (\text{FeO}) \cdot \% [\text{Mn}]) \quad 3.16$$

Fe is large compared to manganese and therefore a constant included in K_{Mn} . Percentages are used because MnO and FeO behave ideally and since the mol. wt. of Fe and Mn are similar,

it is immaterial whether mol. % or wt. % is taken. Here, although manganese is oxidised by dissolved oxygen yet since the latter is related to slag (FeO), the equation above will hold true. The K_{Mn} in the pure and in slag systems has been investigated by numerous workers. Chipman, Gero and Winkler²⁶ give the temperature-function of the constant as

$$\log K_{Mn} = 6,440/T - 2.95 \quad 3.17$$

Recently the following equation has been suggested :¹²⁵

$$\log K_{Mn} = 7,110/T - 3.375 \quad 3.17a$$

From Eq. 3.16 the Mn-content of iron at any temperature is dependent only on the MnO/FeO ratio and not on their absolute values. Therefore, any dilution of the FeO-MnO slag by any component or components which do not affect their ideality will not affect the [Mn] values. But, of course, such a dilution will enable manganese oxidation by a lower oxygen-content of iron. Again, the ratio of manganese in slag and iron expressed by (MnO)/[Mn] depends upon (FeO) and, therefore, on the oxygen-content of iron. In view of the cost of the metal it must be noted that these concentrations are in wt. %; they are not absolute values. The actual quantities of manganese in iron and slag depend upon the total weight of steel bath and slag. This should be taken into consideration in open-hearth where the slag is continuously changing.

The relationship between [Mn] and [O] in liquid iron at various temperatures is shown in Fig. 3.9.²⁷ It is qualitatively similar to that of Körber and Oelsen¹⁰ but based on recent data. Eq. 3.19 used for the calculation has been derived from a combination of Eqs. 3.6 and 3.17.

$$[Mn] + [O] = (MnO) \text{ in } (FeO) \quad 3.18$$

$$\log K = \log (MnO) / (\% [Mn] \cdot \% [O]) = 12,760/T - 5.68 \quad 3.19$$

Strictly speaking, the isothermals in the figure are valid for the range of liquid oxides (Zone I). Zone II is the field of existence of liquid iron and solid FeO-MnO solution. The de-

oxidation curves can be extended into this field from calculations based on FeO-MnO phase diagram (Fig. 3.40a). In zone III, both iron and FeO-MnO are solid.

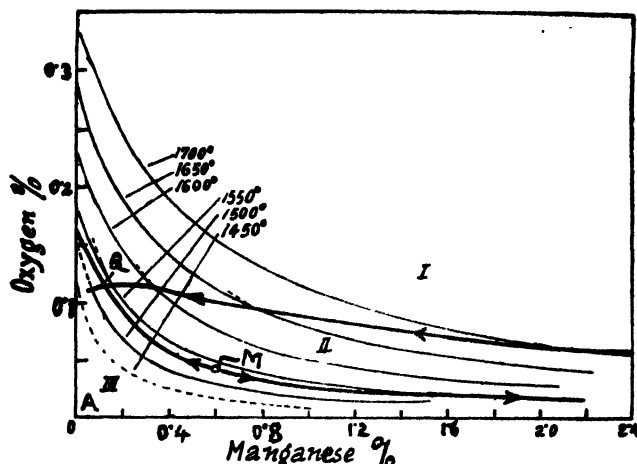


Fig. 3.9—Relationship between manganese and oxygen in pure liquid iron at different temperatures. Zone I, liquid iron & liquid FeO-MnO; zone II, liquid iron & solid FeO-MnO; zone III, solid iron & solid FeO-MnO. (H. Schenck, N. G. Schmahl & A. K. Biswas, *Archiv f. d. Eisenhuettenwesen*, 28, 1957, 520).

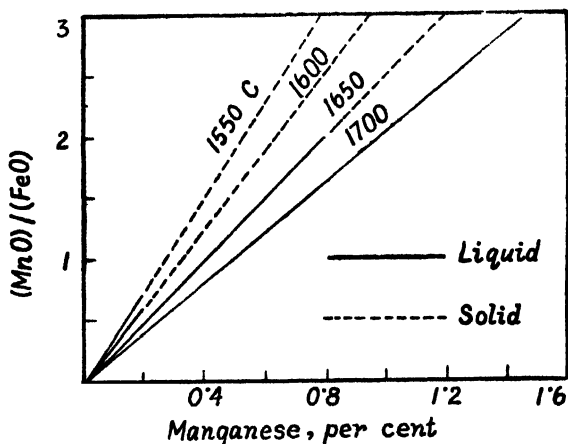


Fig. 3.10—Relation between $(\text{MnO})/(\text{FeO})$ in slag & Mn in metal at various temperatures.

The [O] content decreases with increase in [Mn] but compared to C, Si Al equilibria the oxygen is rather high. At $1,600^{\circ}\text{C}$ and 0.4% Mn, it is $\sim 0.1\%$. Such a high oxygen is ordinarily not present in steel, except perhaps in very low carbon variety under highly oxidising slag. The affinity of Mn for oxygen is not great and, therefore, it is a weak deoxidiser. Fig. 3.9, however, has importance in the deoxidation (by precipitation) of steel. The metal composition, which almost invariably lies in zone III, is such that Mn-O reaction can take place only after the solidification starts. As steel starts freezing, more or less pure crystals of iron separate out initially and the rest metallic melt becomes progressively enriched in both manganese and oxygen. Any melt having initial composition on the right of line AM would become strongly enriched in Mn together with separation of solid FeO-MnO as shown by the direction of the arrow. Any composition between AQ and AM will initially form solid oxides and on reaching Q the separation of liquid oxides starts. Left of AQ would always lead to liquid oxides. The point M has been calculated from fractional crystallisation considerations.

While deoxidation by manganese is important especially for the rimming steel, the practically melt always contains some carbon. Therefore, it is proper to consider the Fe-Mn-O-C system which has been discussed in the next section.

From Eqs. 3.16 and 3.17, the ratio of the deoxidation products ($\text{MnO} / (\text{FeO})$) is a linear function of [Mn] as shown by the isothermals in Fig. 3.10. The dotted portions represent the theoretical values because of separation of solid oxides.

From the figure, the manganese-content of slag increases, the higher the manganese present in metal. The influence of temperature is also clear, e.g. say at $1,650^{\circ}\text{C}$ and 1% Mn, the ratio $(\text{MnO})/(\text{FeO})=2.5$. As temperature decreases, the ratio increases or in other words more of Mn goes into slag. Increase of temperature has the opposite effect, i.e. manganese reverts from slag to metal. This reversal of Mn in basic open-hearth process is a sign that the bath is getting hotter and reaching tapping heat. Further, if at any temperature (MnO) exceeds a certain value then solid FeO-MnO instead of liquid will separate out. As for example, such a case will occur, say, at $1,650^{\circ}\text{C}$ at 0.8% Mn and $\text{MnO}/\text{FeO}=2.0$.

Fe—Mn—C—O

It is necessary for an understanding of the manganese-oxygen equilibrium to know how it behaves in the presence of carbon. The latter element is invariably present in steel, however small the amount may be. The equilibrium relation between the carbon and manganese in iron can be found out by interrelating Figs. 3.6, 3.9 & 3.10 for $p_{\text{CO}} = 1$ atm. Such a relation as given in Fig. 3.11 in fact depicts the amount of each that will undergo simultaneous oxidation on introduction of oxygen in Fe-Mn-C alloys. The calculations, however, do not take into account the influence of each of the elements on the activity of the others or of the simultaneous atomic interactions amongst each other. From Fig. 3.11, 0.02—0.04% carbon is in general equivalent to about 1.2% Mn in iron at 1,700°C, i.e. the affinity of manganese for oxygen is much less than that of carbon. The higher the temperature the lower becomes the affinity of Mn for oxygen, whereas that of carbon remains almost same because of the negligible temperature co-efficient of Eq. 3.10. As an example, at 1,600°C with 1.0% Mn, an iron-carbon-manganese alloy can be oxidised to a carbon-content of 0.04% before oxygen starts its action on Mn. At 1,700°C the same alloy can be decarburised to a value 0.025%C. If such an oxidation takes place at low pressures or in the bottom-blown converters ($p_{\text{CO}} = 0.45$ atm.) the corresponding % [C] will be still lower.

The equilibrium oxygen in Fe-Mn-O system becomes less if the MnO formed gets diluted, or its activity lowered by compound formation. As such, if during the oxidation, there occurs a dilution e.g. by the fluxing of the refractories, then a manganese oxidation can take place even at low oxygen levels caused by the presence of carbon. Manganese will eventually distribute itself between the slag and metal. Fig. 3.12 shows the relation between % [C] and (MnO)/[Mn]. The higher the [C] the lower is the ratio which means that the carbon in steel bath inhibits the oxidation and slagging of manganese.

The Fe-Mn-C-O system assumes great importance in rimming steels. The rimming action and the formation of liquid or solid FeO-MnO slag in ingots depend upon the [Mn], [C] & [O] contents.

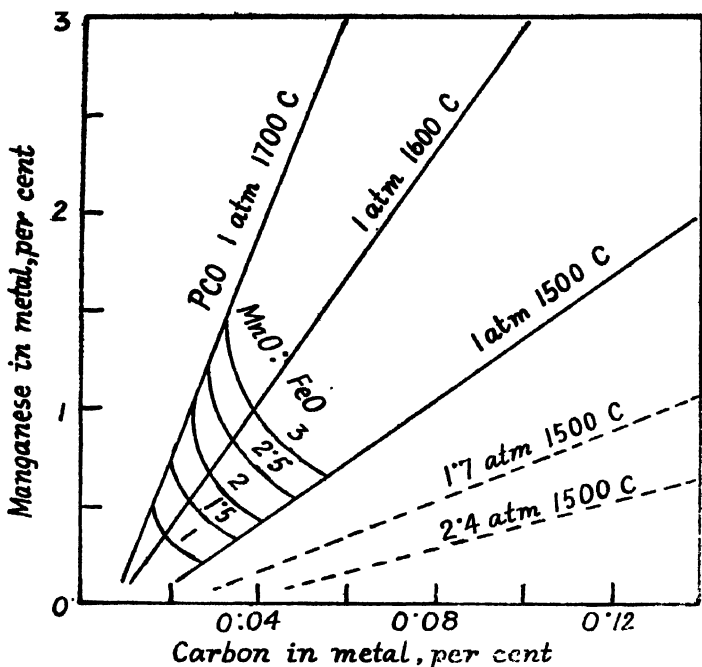


Fig. 3.11—Equilibrium relationship between C & Mn in metal at different temperatures.

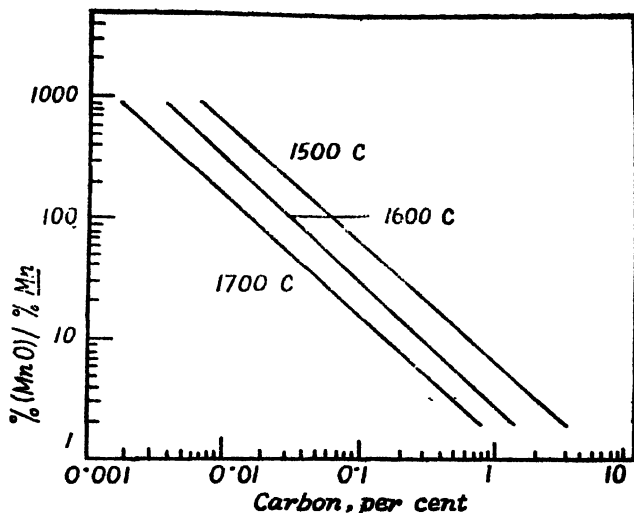


Fig. 3.12—Relation between $\frac{\text{(MnO)}}{[\text{Mn}]}$ & $[\text{C}]$ in liquid iron at various temperatures.

The affinity of manganese for oxygen is not great. Carbon has much greater affinity and, therefore, as long as sufficient carbon is present the [O]-content is determined not by manganese but by carbon. Only in case of rimming steels where carbon is very low, is there an approach to an equilibrium relation between Mn and O after pouring in the casting ladle. C-O reaction in the ladle is inhibited by the lack of nucleation facilities for CO-evolution.

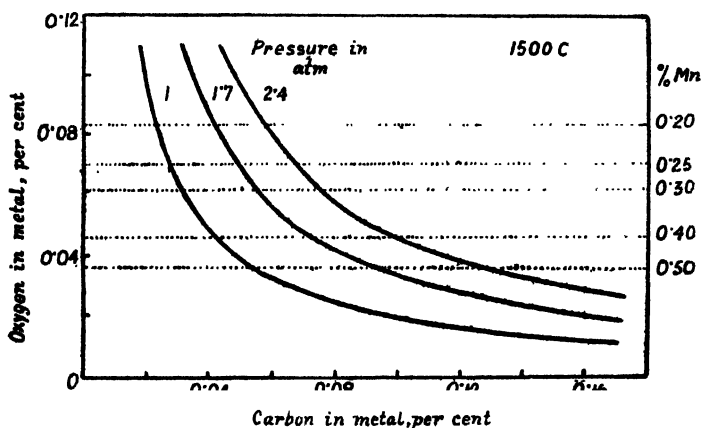
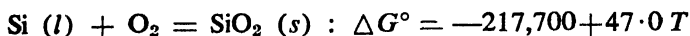


Fig. 3.13—The deoxidising action of carbon & manganese at different ingot depths at 1500°C. (K. Kupzog, R. Hammer & H. Rellermeyer, *Stahl und Eisen*, 82, 1962, 396).

The significance of Mn and C contents in rimming varieties becomes apparent only when the steel is poured into ingot moulds. These are the two foreign elements which take part in the reaction with oxygen. As the metal in ingots starts freezing, more or less pure crystals of iron begin to separate out and the liquid portion or the rest metallic melt becomes progressively enriched in Mn, C and O. Carbon and manganese will react as soon as oxygen in the metal exceeds the corresponding equilibrium values. The iron crystals act as nuclei for the CO-evolution; whereas, the C-O reaction is inhibited by the ferrostatic pressure of the ingot head. The equilibrium [C] & [O] contents at the depth of 0 m, 1 m, and 2 m (equivalent to 1 atm., 1.7 atm. and 2.4 atm. respectively) are shown for 1,500°C in Fig. 3.13.²⁸ It can be seen that for the same C, there is considerable oxygen build-up at

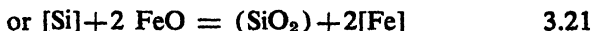
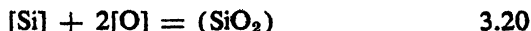
higher pressures, i.e. with increasing ingot depth. With progressive enrichment of the residual melt in these elements, CO will evolve when [O] exceeds the equilibrium value, which depends on the extent of ferrostatic pressure. If the simultaneously increasing [Mn]-concentration exceeds the equilibrium value with respect to oxygen before the conditions necessary for carbon boil or the so-called rimming action are reached, then the C-reaction will not occur and manganese will react with oxygen to form liquid or solid deoxidation products according to the proportion of MnO : FeO, as given in Figs. 3.10 and 3.40a. That is why most of the ingot slags originate at the bottom where manganese is in a more favourable position than carbon to act as a deoxidising agent.

The above is made clear from Fig. 3.13. Here the equilibrium isotherms of carbon reaction at three different pressures (as mentioned above) are drawn for 1,500°C together with those for manganese. One can now deduce the concentrations and ingot depths at which the Mn-deoxidation may affect the carbon reaction. In the liquid portion of the solidifying ingot for manganese content of 0.35%, the carbon should be more than 0.04% in order that steel may rim from the beginning. For the same Mn and at a depth of 1 m (i.e. 1.7 atm. pressure), C should be above 0.06% for the rim; at lower C, deoxidation will be effected by the manganese. The ingot slag can be avoided, even at the bottom if C exceeds 0.09%, so that the C-O reaction may precede manganese deoxidation reaction.



m.p. of Si & SiO₂ = 1,700° & 1,986°K respectively.

In any experiment dealing with the oxidation of silicon alone in iron the container which holds the liquid iron-silicon alloy must be of pure silica; any other refractory would corrode and dilute the slag, FeO-SiO₂, formed during oxidation, with foreign matter. As with manganese and carbon, the presence of silicon lowers the solubility of oxygen in iron. The Fe-Si-O equilibrium is given by :



Since the slag is saturated with silica its activity may be taken as constant. The temperature functions of the respective equilibrium constants are⁵ :

$$\log K_{\text{Si}} = \log [\text{O}]^2 \cdot [\text{Si}] = -19,050/T + 5.750 \quad 3.22$$

$$\log K'_{\text{Si}} = \log (a^2_{\text{FeO}} \cdot [\text{Si}]) = -6,410/T + 0.0282 \quad 3.23$$

It is worthwhile to mention here that the oxygen-content of pure liquid iron under silica-saturated FeO-SiO₂ slag is only a function of temperature,

$$\log \% [\text{O}] = -6,120/T + 2.212 \quad 3.24$$

Therefore, the amount of silicon present in iron under the same slag will also be a function of temperature only, given by :

$$\log \% [\text{Si}] = -6,810/T + 1.326 \quad 3.25$$

If iron contains more silicon at any temperature than given by the above equation, solid silica will separate out.

Fig. 3.41 is a FeO-SiO₂ phase diagram where the saturation line shown is different from that of Bowen and Shairer. The figure shows that the saturation line deviates only slightly from vertical and, therefore, the saturation values do not change considerably with temperature, e.g. about 2-3% at steelmaking temperatures.

The isothermals of silicon-oxygen reactions are shown in Fig. 3.14. The equilibrium relations show that for 1% Si in iron, the corresponding oxygen is 0.006% and for 0.20% Si the oxygen is 0.014% at 1,600°C. The curves become steeper afterwards and the equilibrium oxygen values rise steeply with decrease of silicon. Fig. 3.15 is an enlargement of Fig. 3.14 at low silicon contents. Here a line is drawn which shows the zone of existence of solid silica and liquid iron silicate. At 1600°C a liquid iron silicate will form only if silicon concentration lies below about 0.005%. Above it, only solid silica will always separate out. Only when Si < 0.005%, there will be enough oxygen in the metal that will furnish FeO for the liquefaction of SiO₂. But the

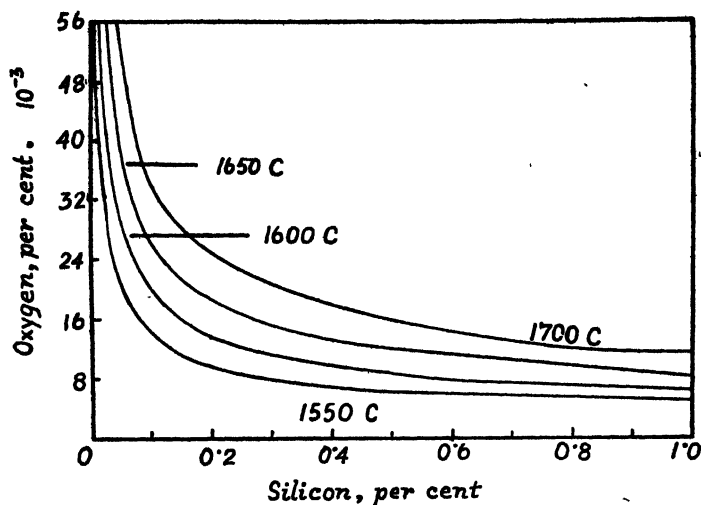


Fig. 3.14—Equilibrium between oxygen & silicon dissolved in liquid iron at different temperatures. Fe-Si-O system.

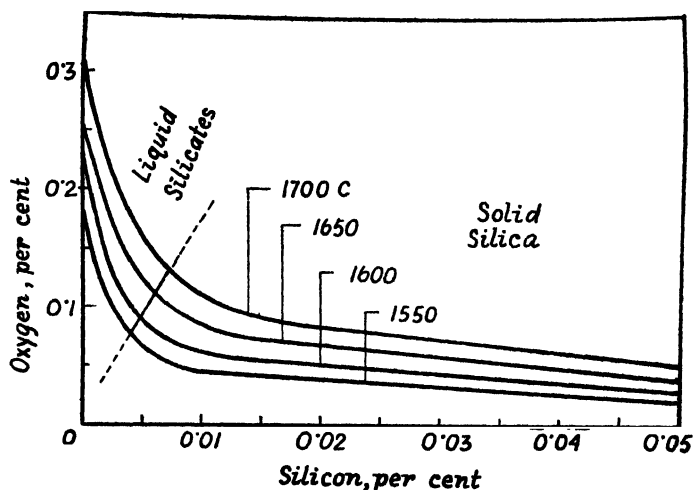


Fig. 3.15—The zones of formation of solid silica and liquid iron silicate in Fe-Si-O system.

slag will remain saturated with silica, the container supplying the necessary SiO₂ for the saturation.

The behaviour of the isothermals with regard to temperature is similar to that of manganese. That is, they shift upwards with temperature which means, for a given Si, more of oxygen will

be in iron the higher the temperature or for a given oxygen more silicon can exist in equilibrium without forming any slag. The maximum silicon value for the formation of liquid silicate will also increase, e.g. about 0.0075% Si at 1,700°C.

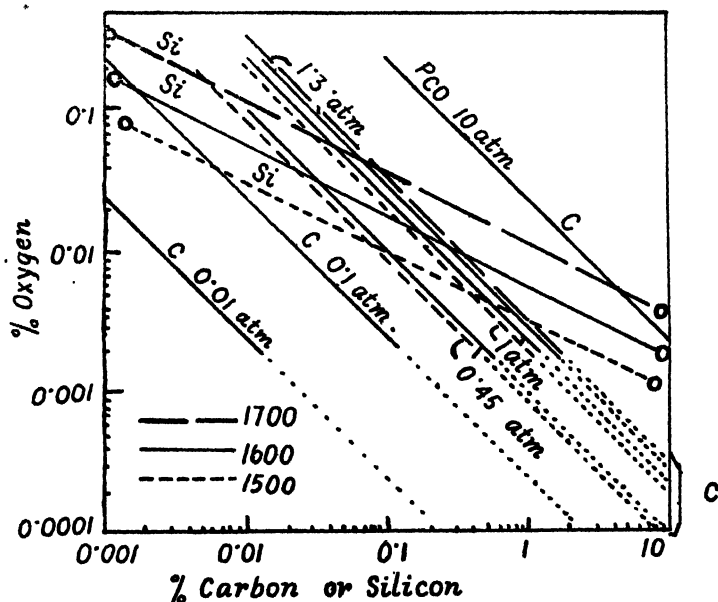


Fig. 3.16—Equilibria between carbon & oxygen as well as between silicon & oxygen in liquid iron at different temperatures and partial pressures of carbon monoxide.

$Fe-Si-C-O$ ³⁴ *

It is apparent that during the oxidation of Fe-Si-C alloy under equilibrium conditions, the equilibrium reactions Fe-Si-O and Fe-C-O themselves must be in equilibrium. A pre-condition must, however, be that the presence of carbon and silicon do not affect their relations with oxygen, i.e. they do not affect or influence their own activities or the activities of iron and oxygen other than those in their respective systems. Under such conditions the oxidation of carbon and silicon will take place independent of the phases of the other system (carbon reaction gives CO-gas phase and

* In this section, the elements Fe, Si, C & O, where they are not inside the bracket [], mean they are in solution in steel.

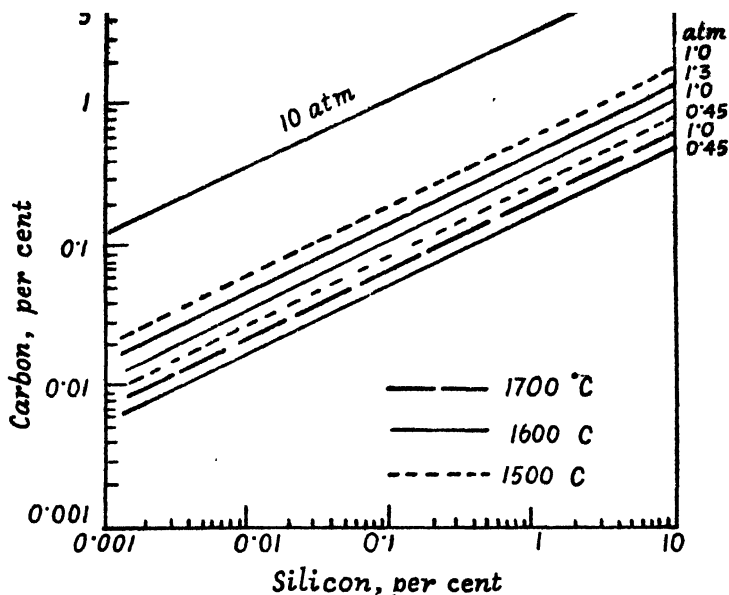


Fig. 3.17—Equilibrium between carbon and silicon in Fe-Si-C-O system at different temperatures and partial pressures of CO.

silicon reaction gives liquid or solid slag). Figs. 3.16 and 3.17 give their relations with respect to oxygen and to themselves respectively. The values for carbon for $p_{\text{CO}} = 0.45$ and 1.3 atm. are also given to correspond with converter and open-hearth practice. From Fig. 3.16, at 1600°C and $p_{\text{CO}} = 1$ atm., 0.5% C corresponds to 0.005% O and 0.5% Si to 0.009% O. In this case, carbon determines the oxygen-content of iron. Oxidation of such an alloy leads to carbon reaction first till it is reduced to 0.28% C = 0.009% O. Further oxidation will mean simultaneous reaction of both and will follow the corresponding curve in Fig. 3.17, on the assumption that the temperature remains constant. In practice, however, specially in converters, the temperature increases continuously and, therefore, the C-Si-O equilibrium relation must change accordingly. It is easy to follow the relation between C & Si from this figure. If, for given temperature, Si-content and p_{CO} , the C-content lies above the respective curve, then an introduction of oxygen in the system (through slag in open-hearth or through air or oxygen in converters) will lead to

decarburisation until the curve is reached, Si remaining the same. Thereafter, the oxidation of C and Si will be simultaneous, their contents at any instant being given by the respective co-ordinates. If the C-content lies below the line, the Si undergoes oxidation at first and when its concentration reaches the point on the line corresponding to the C-content, both start being oxidised simultaneously.

As mentioned before, the temperature function of C-O reaction is small. But the influence of temperature on Si-O equilibrium is very strong. From Figs. 3.16 and 3.17 it is clear that higher the temperature the more stable is silicon against oxidation. In other words, for any given C- & Si-contents, the oxidation of silicon will start earlier at lower temperature than at higher one. This phenomenon has great practical significance in Bessemer converter. If iron is hot and contains much of silicon, its oxidation will raise the temperature of the bath greatly, the result being a stage will be reached where decarburisation will start before complete desiliconisation. At the end of the heat some silicon will be left in the bath which will be a burden in open-hearth where duplexing is in vogue. If the partial pressure of CO is low as in converters, it will act in the same sense as increase of temperature and, therefore, desiliconisation will be suppressed as compared to decarburisation.

*Fe—Si—Mn—O **

This system is of supreme importance not only in the production of acid steel but also in the deoxidation of finished liquid steel and separation and removal of the insoluble silicates. It is intended, therefore, to treat this system in detail as we have to refer to this system frequently when dealing with acid steelmaking and deoxidation. We have already considered the relations between Mn or Si and oxygen separately while discussing the equilibria of the Fe-Mn-O and Fe-Si-O systems. It has been found experimentally and corroborated by many,^{5,30,31} that the oxygen content of iron in presence of Mn and Si in equilibrium is much less than that when Mn or Si are present alone. This is probably because of a decrease in the activity of slag MnO, which is bound

* In this section, the elements Fe, Mn, Si, & O, where they are not inside the bracket[], mean they are in solution in steel.

strongly as silicate. This system was studied extensively by Körber and Oelsen.³⁰ Although the oxygen-contents found by them are rather on the high side, this work enables one to grasp the simultaneous action of Mn and Si on oxygen in iron and *vice versa*.

A knowledge of the acid slag system FeO-MnO-SiO_2 is necessary for understanding the treatment in this section. From Fig. 3.19a the solubility limit of SiO_2 for pure FeO-MnO-SiO_2 slag is about 50%- SiO_2 . At this limit the slag is very viscous. The viscosity decreases as the % SiO_2 decreases below the limit. If SiO_2 is added to an already silica-saturated (line *a-b*) FeO-MnO slag it does not dissolve but remain as solid SiO_2 as a separate phase. In acid steelmaking or in laboratory experiments in silica-crucibles the slag is always saturated with SiO_2 since there is a constant supply of SiO_2 from the furnace lining or the crucible whenever the simultaneous reactions of Fe-Si-Mn-MnO-FeO bring the SiO_2 content below the solubility limit.

The laboratory experiments of Körber and Oelsen should not apply to actual acid steelmaking except perhaps to very low carbon steels, since carbon exhibits a reducing action on the various oxides and this reaction determines the equilibria of the constituents of slag. The influence of carbon on Fe, Mn and Si equilibria under silica-saturated FeO-MnO slag is dealt with in the next section. Nevertheless the behaviour of Si and Mn in carbon-free melt forms the basis for a clear understanding of the action of carbon on Fe-Mn-Si-O system.

The reaction of Si and Mn in carbon-free melt constitutes the equilibrium between Si and Mn in the steel bath, FeO-MnO-SiO_2 slag and solid silica. The relevant equations are :



Körber and Oelsen have given in Fig. 3.18 the relation between the constituents in slag and bath. Since oxygen in bath and FeO in slag are inter-related by partition law (at $1,600^\circ\text{C}$, % $[\text{O}]/\% (\text{FeO}) = 0.0021$), the values of oxygen are also given. SiO_2 is taken as 50% and $(\text{FeO} + \text{MnO}) = 50\%$. From the starting

point of the ordinate, i.e. $[\text{Mn}] = 0\%$, the slag contains a large amount of FeO and the $[\text{Si}]$ is small. The steep rise of the slag isotherm shows that on addition of small amount of Mn , the slag is rapidly enriched with MnO . As Mn increases, the slag FeO is fast replaced by MnO . Simultaneously with the increase of Mn , the Si -content also increases, at first slowly then rapidly. Since the $[\text{O}]$ is controlled by $[\text{O}]/(\text{FeO}) = \text{constant}$, the oxygen in the bath decreases as FeO -slag decreases. The constant does not alter appreciably even when the constituents of slag and steel vary considerably or small quantities of CaO and Al_2O_3 are present. (FeO in slag, however, does not behave ideally, its activity changes with SiO_2 , MnO , Al_2O_3 , CaO , etc. in slag.)

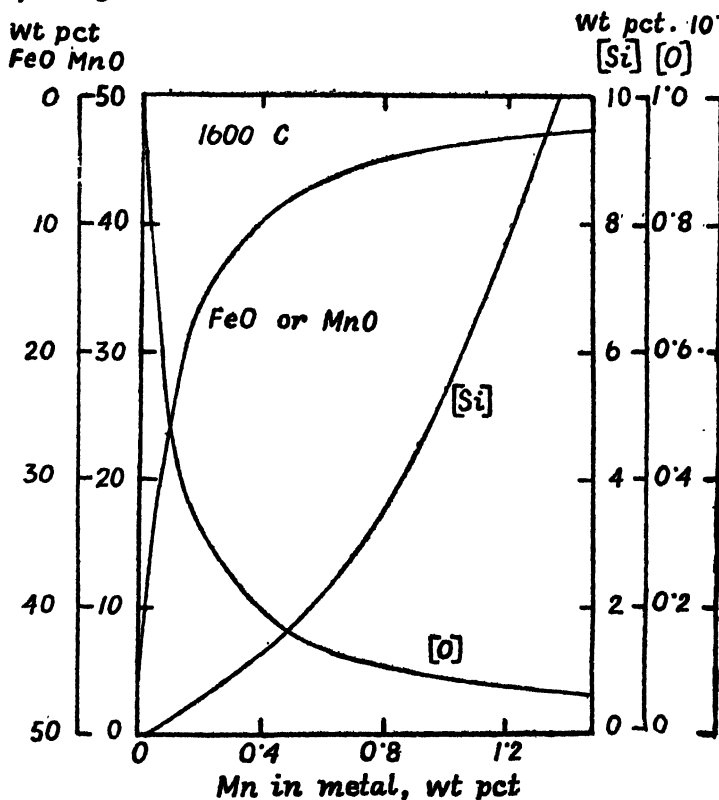


Fig. 3.18—Equilibrium between liquid iron and silica-saturated iron-manganese-silicate at 1,600°C.
(Körber & Oelsen).

It is clear from the figure that at a given temperature and given Mn-content (under FeO-MnO-SiO₂ slag saturated with silica) all the constituents in slag and also Si are fixed. If Si lies below the Si-isotherm under these conditions, the bath will react with SiO₂ resulting in the reduction of Si to the bath and formation of FeO-MnO-silicate. The reduction ceases when Si-content reaches the Si-isothermal. When Si lies above the isothermal, manganese and iron are without action against SiO₂, rather silicon reduces the FeO and MnO of slag until the equilibrium given by the isothermal is reached or the two oxides disappear completely, whichever is earlier. In such a case the slag is completely transformed into solid SiO₂.

The isotherms in Fig. 3.18 are valid for 1600°C. The equilibria, however, are functions of temperature. The influence of temperature is such that for a given slag composition, a decrease in temperature decreases the oxygen, manganese and silicon contents of the bath or, in other words, decreasing temperature facilitates the slagging of Si and Mn and lowering of bath oxygen (deoxidation). On the other hand, at a given Mn-content, the (FeO-, [O] and [Si] contents of the slag and bath increase with increasing temperature.

At about 1600°C if the slag contains less than 50% silica, a good liquid silicate will result, whereas above 50% it will be a heterogeneous mixture of liquid silicate and solid silica. Silica is soluble in FeO-MnO-SiO₂ melt only to a limited extent ranging from 50 to 65% according as impurities like CaO, Al₂O₃ are present. This limited solubility enables the melting of steel in acid lining and with such a lining no melt with a slag under line *a-b* of Fig. 3.19*a* is possible. It is, however, imperative that at any temperature and at any slag composition (under the line *a-b*) in equilibrium with an iron melt, there must be definite oxygen, manganese and silicon contents in the metal.

The equilibrium reactions occurring in the experiments of Körber and Oelsen and also in acid steelmaking, belong to a three-phase system, the phases being metal, slag and solid SiO₂. The important question is whether solid silica (m.p. $\sim 1,710^{\circ}\text{C}$) does also take part in the reactions. They assume that at steel-making temperatures of 1,600°—1,650°C, the m.p. of SiO₂ is nearly approached and, therefore, solid SiO₂ takes an active part

in the reactions. The participation of solid SiO_2 in the metal-slag reactions leads to the reaction $(\text{SiO}_2) + 2[\text{Mn}] = [\text{Si}] + 2(\text{MnO})$, the temperature function of the equilibrium constant being small: $\log K = 3,177/T - 4.757$. At steelmaking temperatures, the relation $[\text{Si}] = 1,200 ([\text{Mn}]/(\text{MnO}))^2$ can be assumed to be valid for all purposes (at $1,600^\circ\text{C}$, $K = 1,200$); or $\sqrt{[\text{Si}]}$ is proportional to $[\text{Mn}]/(\text{MnO})$, the proportionality constant being 34.7.

This negligible influence of temperature has a significance in acid steelmaking where the principal aim is silica reduction and increase of Si in the bath. Such an aim can only be realised if (FeO)-slag is kept low so that the principal reactants are Si and Mn and their oxides in slag. If higher Si is to be obtained from a reduction of solid SiO_2 by Mn-containing bath than corresponding to Si-isotherm, it can only be possible either by the reducing action of carbon or by diluting the slag by an oxide, viz. CaO, which increases the solubility of SiO_2 considerably in the silicate slag. Naturally, such a slag must also be saturated with silica.

Fig. 3.18 shows that for a given Mn-content all other constituents in the metal and slag are definite and fixed. This is made possible because of simultaneous saturation of metal and slag with solid SiO_2 . At any temperature one of the concentrations of Mn, Si, O, (MnO) or (FeO) determines all others. If, however, the metal and the slag remain unsaturated with silica, the isothermals can no longer be drawn on a plane surface and a space model has been devised by Körber and Oelsen.³⁰ Here Mn, Si and O are the three co-ordinates and the composition of slag is difficult to incorporate.

Fig. 3.19 gives the projection of the three views of the model, viz. plan, elevation and side-view at 1600°C . Each will be taken separately and discussed.

Plan: The line $G'F'$ corresponds to the relation of Mn and Si in a bath in equilibrium with silica-saturated FeO-MnO-silicate. In the region above $G'F'$ only solid silica is possible in presence of the metal, whereas below the line only unsaturated liquid silicate exists, solid silica being absent. Along the line $G'F'$ itself the stable phases are: metal, slag and solid silica. The lines of constant oxygen-contents above $G'F'$ show that they are dependent only on the Si-content and Mn has no influence whatsoever. The

opposite is nearly true in the region below $G'F'$ where O-content runs parallel to Si-content. At low silicon the lines of constant O-contents bend towards higher Mn-content. When the Mn and Si-contents cross the bends above these points, then for a given Mn-content, the increasing Si no longer decreases the O-content. Only when the line $G'F'$ is reached, further addition of silicon decreases the oxygen with the formation of solid silica. Let us endeavour to find the significance of this diagram. An iron alloy with about 0.95% Si and about 0.5% Mn is in equilibrium with 0.006% O. If oxygen is introduced to such a system it will start oxidising silicon to solid SiO_2 and the oxygen content of the alloy will increase parallel to the Si-co-ordinate and perpendicular to Mn-co-ordinate at 0.5% Mn. When the line $G'F'$ at 0.015% O is reached, corresponding to 0.16% Si, the simultaneous oxidation of manganese and silicon will start and follow $G'F'$ thereafter.

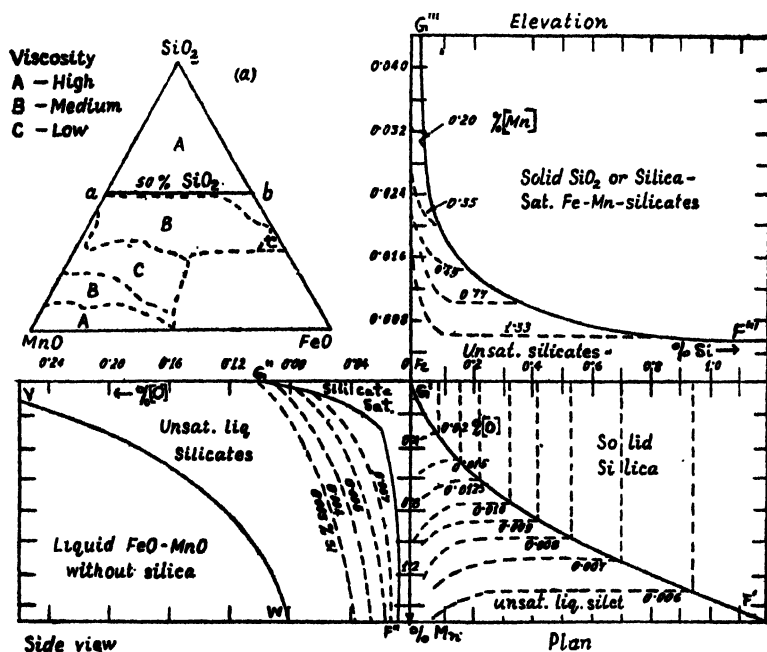


Fig. 3.19—Elevation, plan & side-view of deoxidation diagram for manganese and silicon at 1,600°C. (Körber & Oelsen). (a) Viscosities of FeO-MnO-SiO_2 slag at 1,600°C, the line 'ab' showing silica saturation.

The slag composition can also be derived with the help of Fig. 3.18. At first only solid silica will be formed. Only at 0.16% Si and 0.5% Mn, the formation of saturated manganese silicate will start which would contain about 8% FeO (from Fig. 3.18) corresponding to 0.015% O. As oxidation of Si and Mn proceeds, the iron melt will pick up more and more of oxygen and FeO in slag will correspondingly increase along the saturated boundary line of FeO-MnO-SiO₂ system (Fig. 3.19a). Although the new slag formed is liquid yet it is saturated with silica and, therefore, the original solid silica formed will not be fully dissolved. Such a slag can have no corroding action on silica lining.

The situation, however, becomes different if the alloy at the start is such that on oxidation its constituents form liquid slag. This happens when Si and Mn lie below $G'F'$. The unsaturated slag formed would react with the lining and manganese and silicon will not be in equilibrium with the furnace lining till the line $G'F'$ is reached. The reaction may be something as follows : for an iron alloy with say 0.4% Si and 1.2% Mn, an oxidation will lead to the formation of a liquid unsaturated silicate, which would absorb silica from the lining till saturation. Such a slag will, however, not be in equilibrium with the melt and it will oxidise manganese to MnO which will immediately react to form saturated manganese silicate. The oxidation of Mn is performed by silica which is reduced to silicon and goes over to the melt, $Mn + SiO_2 = MnO + Si$. From the equation, oxidation of 1% Mn is equivalent to reduction of 0.255% Si into the melt. Therefore, as oxidation of Mn proceeds and the line $G'F'$ is approached, the composition *vis-à-vis* Mn and Si of the melt will not reach the line at 0.4% Si but at somewhat higher values. Thereafter, simultaneous oxidation of both the elements will follow $G'F'$. The composition of the slag where $G'F'$ is met will be given by the oxygen-content given in Fig. 3.18. The change of slag composition along $G'F'$ is found in the same way as in previous case.

Side-view : It is the same as the Fe-Mn-O isothermal at 1,600°C. The liquid unsaturated silicate exists in the wide zone between VW and $G''F''$. The strong action of silicon on the oxygen-content of liquid iron containing manganese is evident

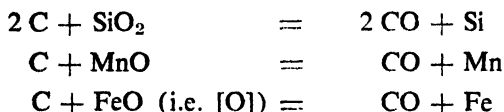
from the figure. The curve $G''F''$ represents the border of saturated and unsaturated silicates at $1,600^{\circ}\text{C}$, i.e. it gives the minimum oxygen-content of the melt capable of furnishing liquid silicates.

Elevation : The curve $G'''F'''$ represents the isothermal of Fe-Si-O at $1,600^{\circ}\text{C}$. The zone of unsaturated liquid silicate lies below this curve. The influence of manganese on the oxygen-content of liquid iron-silicon alloy is again evident. When Si, Mn and O in iron lie below $G'''F'''$, fluid silicates are invariably obtained.

Hilty and Craft³¹ have given recent data on the influence of Mn on silicon deoxidation (*e.f.* Fig. 3.32*b*). The recent work of Schenck and Wiesner on Fe-Mn-Si-O system has been discussed on p. 246.

Fe—Mn—Si—C—O*

The Fe-Mn-Si-O system described in the previous section is important from the point of view of deoxidation but it does not fully depict the equilibrium relations in acid steelmaking. Carbon is invariably present in all steels and it takes part in the reaction as a strong reducing agent. The reaction of carbon with oxygen in steel and oxides in the slag will evidently affect the equilibria in the preceding section. The reactions are as follows :



Apart from the 3 phases in the previous section, e.g. liquid metal, slag and solid SiO_2 , we have here a fourth phase, gaseous CO. According to Körber and Oelsen, when the equilibrium is reached and if liquid slag is present, then at any given temperature and for any fixed Mn-content in liquid melt there must be :

- (i) definite Si-, C- and O- contents in the melt
- (ii) definite (FeO) & (MnO)-contents in the slag
- (iii) a definite p_{CO} in CO-bubbles in the melt

* In this section, the elements Fe, Si, Mn, C & O, where they are not inside the bracket [] mean they are in solution in steel.

We have seen (Fig. 3.16) that at any temperature there is a definite C-content in equilibrium with a given O-content. For $1,600^{\circ}\text{C}$ and $p_{\text{CO}} = 1$ atm. the relation is $[\text{C}].[O] = 0.0025$. The relation varies with the partial pressure of carbon monoxide. Since for given Mn and Si-contents in liquid iron under silica saturated liquid silicate there is a definite amount of O in equilibrium, the C-content in equilibrium must also be definite, given by the above relation. As for example, from Fig. 3.19, it can be seen that 0.7% Si and 1.12% Mn are in equilibrium with 0.007% O. Therefore the %C in equilibrium will be $0.0025/0.007 = 0.36\%$. If such a melt contains higher carbon, then oxygen, on introduction in the system, will react with carbon first and when

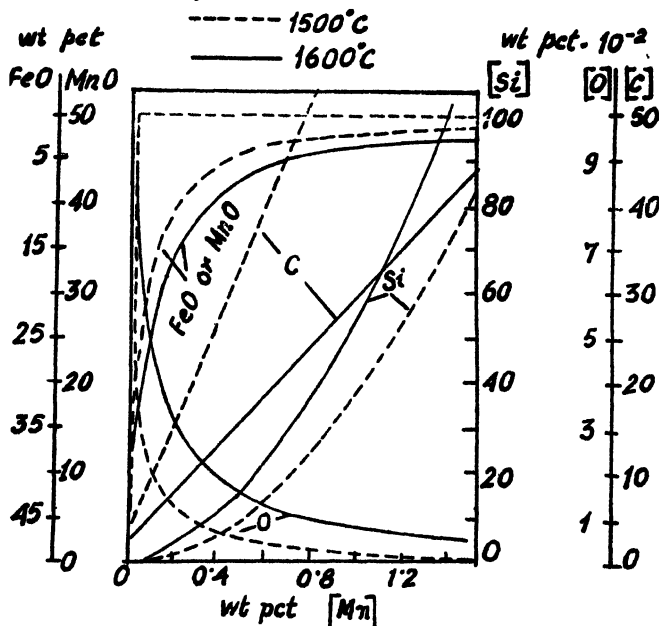


Fig. 3.20—Equilibrium between liquid iron containing carbon, manganese & silicon and silica saturated FeO-MnO-SiO_2 slag at $1,500^{\circ}\text{C}$ & $1,600^{\circ}\text{C}$.
 $p_{\text{CO}} = 1$ atm (Korber & Oelsen).

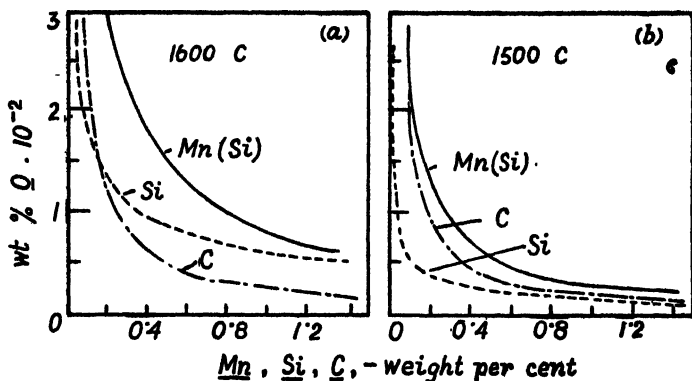
the excess of it is removed and carbon reaches 0.36%, the simultaneous oxidation of Mn, Si and C will start. When 0.22% Si and 0.6% Mn ($= 0.0125\%$ O) are reached, the carbon in

equilibrium will be $0.0025/0.0125=0.2\%$, and so on. If the initial C-content is less, Mn and Si will suffer oxidation first and move along $G'F'$ until oxygen in iron increases and becomes equivalent to the given carbon. Thereafter, all three elements will be oxidised simultaneously. If say $C=0.2\%$, $Si=0.7\%$ and $Mn=1.12\%$, then decarburisation will start when Mn and Si reach 0.6% and 0.22% respectively.

Fig. 3.20 has been derived by Körber and Oelsen³² from Vacher and Hamilton's $[C].[O]=0.0025$ at 1600°C for $p_{\text{CO}}=1$ atm. It is clear how the equilibria of slag, silicon and oxygen are influenced by carbon. If for a given Mn-content the C-content is higher than the C-curve, then carbon will react with the slag and silica until a lower carbon value is reached. Such a reaction would, however, mean a reduction of Mn and Si to iron until all the constituents of slag and metal are in equilibrium. When carbon is above the C-curve it is not possible for Si, Mn and Fe and the oxides in the slag to be in equilibrium with one another. The reaction of Fe, Mn and Si with their oxides cannot remain in equilibrium if carbon is not also in equilibrium with these oxides. No decarburisation or CO evolution can take place if C-content lies under the C-curve. It can only happen when the oxygen-potential of the slag is raised or the partial pressure of CO is lowered by melting under vacuum or by passing inert gases like argon, nitrogen through the melt.

It can be ascertained from Fig. 3.20 how far carbon can be lowered for any given Mn- and Si-contents. Under a (FeO)-poor silicate with 5% (FeO) and with $[Mn]=0.8\%$ & $[Si]=0.38\%$, the C-content can be lowered to 0.24% . It can be lowered to $\sim 0.024\%$ when working under 50% (FeO) corresponding to $[O]=0.105\%$.

These equilibrium reactions suffer considerable changes with temperature. The C-curve at $1,500^{\circ}\text{C}$ runs at a steeper angle. It has been calculated from $[C].[O]=0.0020$ at that temperature.³³ For the same manganese and silicon as in the preceding paragraph, the carbon content cannot be lowered below 0.53% at $1,500^{\circ}\text{C}$ whereas at $1,600^{\circ}\text{C}$ it was 0.24% . The lower reducing action of carbon on silicate and silica, i.e. the higher stability of the slag with decreasing temperature is clear from Fig. 3.21³². At $1,500^{\circ}\text{C}$ the oxidation of silicon is favoured more than that of

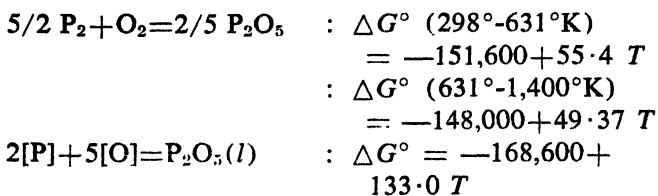


[The underlined elements denote their percentages in steel.]
 Fig. 3.21—Comparison of deoxidising actions of carbon, manganese & silicon in the presence of silica or silicate at 1,500°C & 1,600°C.
 (Korber & Oelsen). For Mn (Si) curve, see text.

carbon, whereas the reverse is the case at 1,600°C. In these figures Mn is drawn against O where manganese has its maximum deoxidising action. It has been found by adding enough silicon to the manganese-containing melt so that a silica saturated FeO-MnO-silicate just starts separating out.

It must, however, be mentioned here that the validity of these equilibria is lost when the melt contains a large amount of carbon. It is because the activity of manganese is lowered by carbon. In other words, for the same silicon more Mn will be required for the formation of liquid silicate. With high carbon, the line $G'F'$ of Fig. 3.19 is brought down, i.e. the zone of solid silica formation is widened.

The equilibrium relations derived for carbon are applicable in the laboratory but not in actual open-hearth practice. The physical process of evolution of CO affects the decarburisation. This will be discussed in Chapter 5.

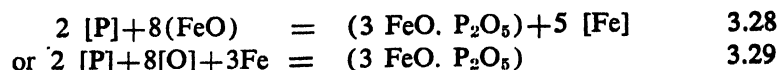


$$K = a_{P_2O_5} / (\% [O]^5 \cdot \% [P]^2) : \log K = 36,850/T - 29.07 \quad 3.27^{35}$$

$$P_2(g) = 2[P] : \Delta G^\circ = -58,500 - 9.1 T \quad (1\% \text{ solution})^{36}$$

The progressive deterioration in the quality of iron ore and coke is continually aggravating the problem of producing quality steel with low phosphorus content. The dephosphorisation of liquid iron is effected by the oxidation of dissolved phosphorus and obtaining the phosphorus pentoxide so formed in the slag in a state of low activity to prevent its subsequent reduction by iron melt.

The reaction in the pure Fe-P-O system takes place according to



Lewenetz & Saamarin³⁷ give the free energy of the reaction and the equilibrium constant of Eq. 3.29 as :

$$\Delta G^\circ = -383,500 + 142.6 T$$

$$\text{and } \log K = 84,200/T - 31.1$$

Fig. 3.22³⁷ shows the relation between phosphorus and oxygen in liquid iron at various temperatures under pure liquid iron-triphosphate slag. The lower the temperature, the lower is the P-content for the same O-content in iron. The figure further shows that oxygen decreases with increasing phosphorus up to

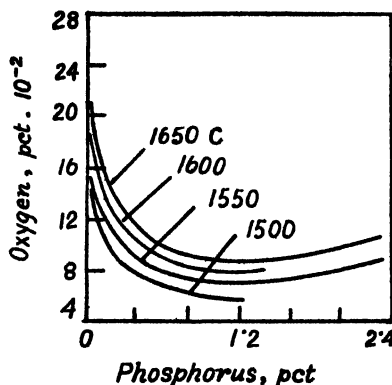


Fig. 3.22—Relation between oxygen & phosphorus contents of iron at different temperatures.

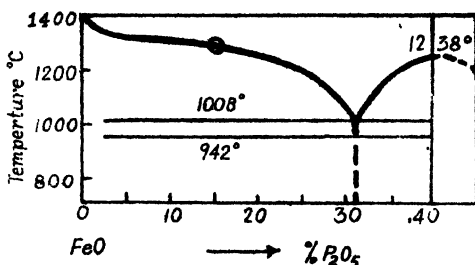
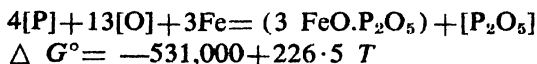


Fig. 3.23—The FeO- P_2O_5 system. (Wentrup).

about 1.2% P, above which it shows a rise in equilibrium oxygen values. This is attributed to the dissolution of P_2O_5 in iron above 1.2% P according to :



This might be an explanation for the fact that in Thomas (basic Bessemer) blow the refining of phosphorus is relatively slow up to about 1.2% P and below this value the velocity of the oxidation is rapid.

The FeO- P_2O_5 system is shown in Fig. 3.23. At about 30.4% P_2O_5 the system forms a eutectic with FeO and 3 FeO. P_2O_5 having a m.p. of $\sim 1008^\circ C^{38}$. The figure shows a flattening of the liquidus curve which signifies a tendency towards separation into two phases, i.e. a tendency towards occurrence of a 'miscibility gap'. In the neighbourhood of about 15% P_2O_5 there is also a distinct change in the run of the curve. This tendency towards immiscibility is of supreme importance in Thomas steel production since the introduction of a foreign substance like lime (CaO) results in an actual separation into two phases.

We will now consider the behaviour of phosphorus in iron under oxidising conditions whereby phosphorus, having a greater affinity for oxygen, goes in larger amounts than iron into the slag. The slag formed out of FeO and P_2O_5 is related to P in iron and their relation, as found by various workers,³⁹⁻⁴² is summarised in Fig. 3.24.

Fig. 3.24 shows the curves when [P] is drawn against (P_2O_5). The experiments of Oelsen and Maetz⁴² were made at $1,600^\circ C$ in MgO-crucibles and those of Schackmann and Krings⁴¹ at $1,450^\circ C$ &

1,525°C in Al_2O_3 -crucibles. While all the curves are similar in shape, that of Maurer and Bishop⁴⁰ is almost a straight line up to about 4% [P]. The other curves appear as if they are not continuous but rather made up of two distinct parts meeting at a definite 'turning point'. This point, which is in the neighbourhood of 15% P_2O_5 , corresponds to the point of inflexion of the liquidus

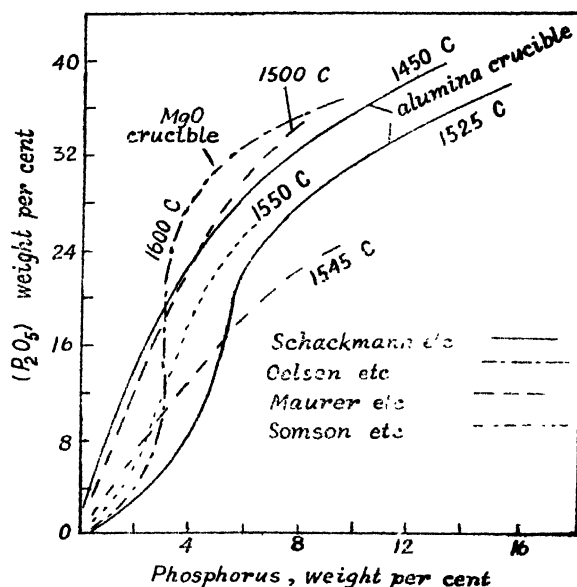


Fig. 3.24—Distribution of phosphorus between liquid iron and pure (FeO) slag. (K. G. Speith & H. V. Ende, *Stahl und Eisen*, 72, 1952, 1998).

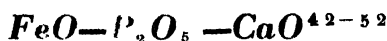
curve of Fig. 3.23. According to Oelsen this 'turning point' is due to the tendency of immiscibility in the iron-phosphate slag. The pronounced 'bend' of Oelsen's curves compared to Schackmann's is due to the presence of MgO which increases the tendency towards immiscibility. CaO behaves similarly but in a much more pronounced manner.

It can be gathered from the curves that the oxidation of phosphorus is relatively slow at lower phosphorus contents than at higher, above the 'bend'. From Oelsen's curve at 1,600°C, 1% [P] is in equilibrium with 1.2—1.4% P_2O_5 i.e. 0.53—0.62%

(P). Therefore, the phosphorus distribution ratio $(P)/[P]$ is less than unity. The ratio becomes more favourable at higher % [P], i.e. at 7.5% [P] the oxide content is 35% or $\sim 16\%$ (P) in the slag, the ratio $(P)/[P]$ being slightly more than 2. Lower the P in iron the lower is the equilibrium (P_2O_5) ; therefore, the higher must be the (FeO)-content. It follows that a low phosphorus content cannot be achieved by the simple oxidation of a phosphorus-containing melt with a tolerable amount of iron oxidised into slag. At steelmaking temperatures the maximum value of the above ratio is about 2 to 3.

A comparison between curves with MgO- and Al_2O_3 -crucibles shows that phosphorus removal into slag in the former case is better. This is because the crucible material enters the slag to a certain extent and basic MgO in the slag favours dephosphorisation.

The influence of temperature can also be seen from a comparison of the curves of Schackmann and Krings at 1,450° and 1,525°C. At lower temperature more phosphorus is removed, which corroborates, as stated before, *that decreasing temperature favours dephosphorisation*.



It has been seen in the preceding section that the removal of phosphorus from iron by oxidation needs a highly oxidising slag or, in other words, a high oxidation potential of the metal. But the extent of phosphorus removal is limited and can be far-reaching only when the phosphorus pentoxide formed is bound with lime into a state of low activity, the combination being calcium tri- or tetraphosphate. Dephosphorisation, therefore, depends on the activities of FeO, P_2O_5 and CaO in the basic slags, the acid processes being incapable of large phosphorus removal in the absence, or in the presence of very little of lime. Although the basic steelmaking slags possess a large number of other constituents, the study of the pure FeO- P_2O_5 -CaO system helps to elucidate the fundamentals of dephosphorisation.

When a certain amount of CaO is incorporated in the FeO- P_2O_5 system or when certain minimum amount of liquid FeO is introduced into tricalcium phosphate at sufficiently high tempera-

tures, they separate into two layers. The upper layer contains essentially the phosphate with a little FeO and the lower one principally FeO with a little of phosphate. The 'miscibility gap' as found by Oelsen and Maetz⁴² in the ternary FeO-P₂O₅-CaO system is shown in Fig. 3.25. They carried on experiments in the neighbourhood of 1,400°C and only iron-rich slag is liquid

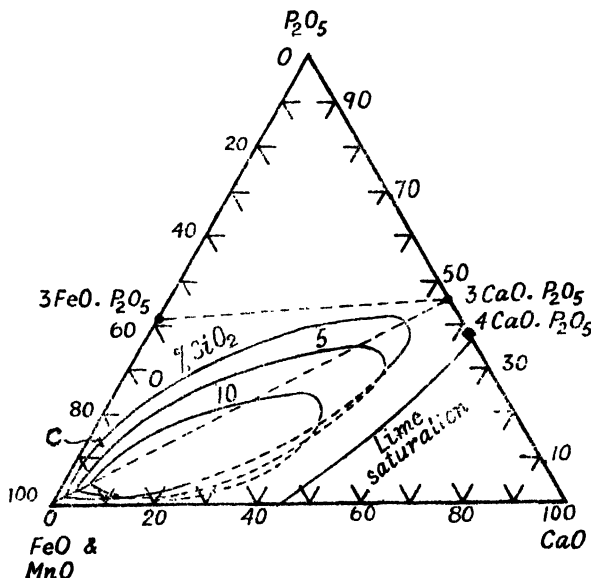


Fig. 3.25—The 'miscibility gaps' in the FeO-P₂O₅-CaO system containing 0%, 5% and 10% SiO₂ at steelmaking temperatures. The lime saturation line is also shown.

at these temperatures. The solid line, therefore, is the experimentally found boundary of the 'miscibility gap' and the dotted line has been assumed by them to form the boundary on the CaO-rich side. Subsequently it has been proved from laboratory and converter experiments that the assumed boundary on the CaO-rich side is largely correct. The line of saturation of the slag with lime is also shown in the figure.

The lines running across through the miscibility gap (cf. Fig. 8.4) are the connodes, their points of intersections on the boundary line giving the composition of the two layers. Outside the lens-shaped gap, the slag is completely miscible and homogeneous. The left hand or FeO-rich and CaO-poor side of Fig. 3.25 shows

that in the lower layer (FeO-rich) CaO decreases at first as P_2O_5 increases and then again increases until the critical point C ($\sim 15\%$ P_2O_5) is reached when the system loses its lower layer character and assumes that of the upper layer. It is to be noted that this critical point coincides with those of Fig. 3.23 and 3.24.

The right hand side of Fig. 3.25 shows the character of the upper phosphate-rich layer. The major amount of lime and P_2O_5 to the extent 30-40% go into the upper-layer. The shape of the 'miscibility gap' shows that at high P_2O_5 concentrations the composition $3CaO \cdot P_2O_5$ is approached, which suggests the probable presence of P_2O_5 as tricalcium phosphate. The importance of the miscibility gap in Thomas slag lies in the increased FeO-activity. As for example, a phosphate layer having 15% FeO is as reactive and as much oxidising to iron as a FeO-layer having 75% FeO because both these layers are in equilibrium. The quantity of each slag variety does not play any role. In other words, the low FeO in a phosphate slag would maintain the same

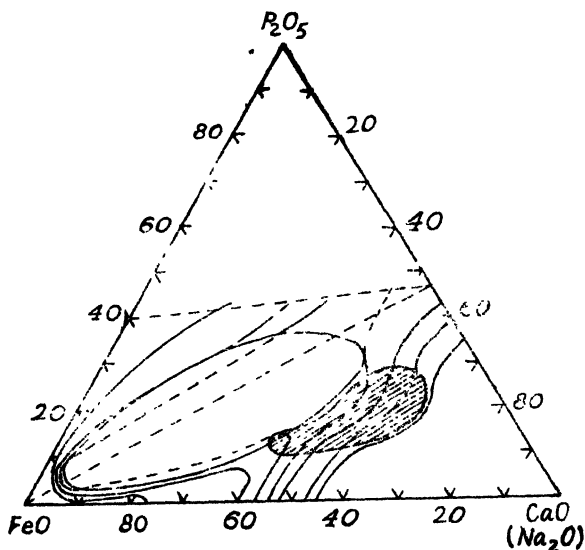


Fig. 3.26—Schematic iso-activity lines of FeO in quasiternary FeO- P_2O_5 -CaO system at 1,600°C. Shaded area shows common Thomas slags. (H. Rellermayer & Th. Kootz, *Stahl und Eisen*, 76, 1956, 965).

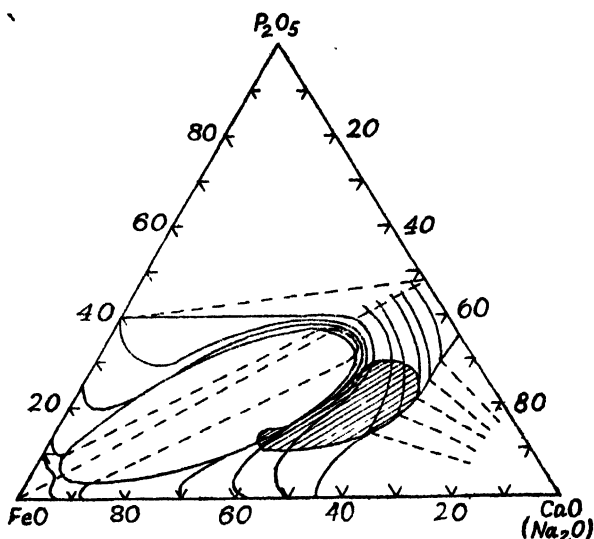


Fig. 3.27—Schematic iso-activity lines of CaO in quasiternary FeO- P_2O_5 -CaO system at 1,600°C. Shaded area shows common Thomas slags. (H. Rellermeyer & Th. Kootz, *Stahl und Eisen*, 76, 1956, 966).

oxygen level in the metal as a highly-rich FeO slag, since the FeO-activity in both the layers, being in equilibrium, is the same. A schematic diagram of lines of similar activities of FeO is given in Fig. 3.26⁵³. *The activity increases as the lines approach the miscibility gap.* The concentrations in the figure have been computed after deducting impurities like SiO_2 , MgO , etc. The shaded area gives the usual slag composition in the Thomas process.

In order to obtain sufficient dephosphorisation of metal, not only a highly oxidising but also a sufficiently basic slag is essential. Lime is used for the purpose of holding P_2O_5 in a strong bond and in a lower state of activity. Action of lime is stronger, the greater the activity of CaO in such slags. Since the activity of pure lime or a fully lime-saturated slag is the highest, the phosphorus removal will be greatest the nearer the slag is towards lime-saturation, provided of course that the oxidising power of the slag is sufficiently maintained. The curves of similar CaO-activities and the lime-saturation line are shown in Fig. 3.27⁵³. *The lines correspond to increasing CaO-activity as they approach*

towards the saturation-line. The shaded area gives the general Thomas slag composition.

Even in the homogeneous fields of $\text{CaO-FeO-P}_2\text{O}_5$ system, the influence of immiscibility is not lost. Thus, as the slag composition approaches the gap boundary, the activity of FeO increases. Although this increasing oxidising power should help dephosphorisation, it does not do so since the basicity decreases as the slag composition moves farther away from the lime-saturation line with the consequent fall of lime activity. Therefore a compromise has to be made and the usual Thomas slag composition lies in the narrow corridor between the lime-saturation and the gap boundaries.

According to Wentrup,⁵⁴ because of the 'miscibility gap', the increase of FeO -concentration above a certain limit will not only have no effect on further dephosphorisation but rather a rephosphorisation of the iron melt may take place. Crossing of the boundary line into the 'gap' will make the slag incapable of effectively dissolving more FeO . Increasing FeO will result in the separation of the slag into two layers causing a diminution of FeO and CaO from the upper layer. Formation of too much of FeO , therefore, impoverishes the dephosphorising phosphate slag of lime which may cause rephosphorisation of the metal.

The amount of lime, that can be incorporated in the slag, is limited. The lime solubility is hardly more than 10% of the composition of tricalcium phosphate. However, the solubility is affected by FeO -content as well. It reaches its highest value at about 15-20% FeO . It is clear there is only a limited room for increasing the lime content.

Thomas slag does not belong to the pure $\text{FeO-P}_2\text{O}_5\text{-CaO}$ system and small amounts of oxide impurities are always present, viz. manganese oxide, magnesium oxide, aluminium oxide, titanium oxide and sometimes chromium and vanadium oxides.

Influence of other Factors

Silica : Oelsen and Maetz⁴² suggest that the presence of silica in $\text{FeO-P}_2\text{O}_5\text{-CaO}$ system narrows down the 'miscibility gap'. With increasing SiO_2 the gap becomes smaller and smaller until at about 15% SiO_2 it completely disappears. The influence of 5% and 10% SiO_2 is shown in Fig. 3.25.

According to Wentrup,⁵⁴ calcium phosphate remains in equilibrium with lime till about 15% SiO_2 in the slag which suggests that in such a SiO_2 -poor slag the activity of lime does not probably vary much. Above 15% SiO_2 the lime is replaced by calcium silicate and remains in equilibrium with the slag and, therefore, the reactivity of lime decreases. Increasing the content of SiO_2 increases the solubility of lime. But lower the lime-content the higher has to be the (FeO) , with increasing SiO_2 , in order to obtain a sufficiently fluid slag. Fig. 3.28⁵⁵ shows the shifting of lime saturation lines to higher CaO with 4% silica at 1,550°C. The

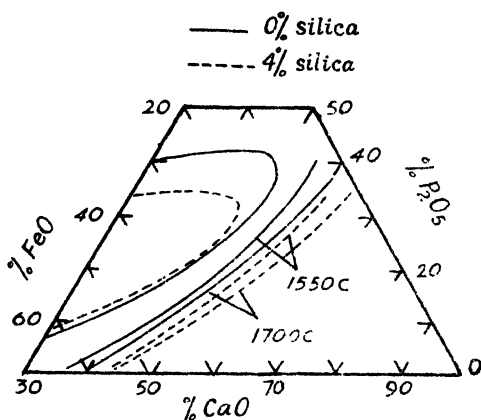


Fig. 3.28—Shifting of lime saturation lines in the $\text{FeO-P}_2\text{O}_5\text{-CaO}$ system with 4% SiO_2 at 1,550°C & 1,700°C. (H. Knüppel & F. Octers, *Stahl und Eisen*, 81, 1961, 1437-49).

amount of shifting ($\sim 4\%$) is equivalent to lime consumed by silica for the formation of $2 \text{CaO} \cdot \text{SiO}_2$.

We will see later (*cf.* p. 111) that with a SiO_2 -rich Thomas slag, the start of slag liquefaction as well as that of dephosphorisation occur later than that with low- SiO_2 slags; the end-phosphorus and oxygen-contents of the melt are also higher.⁵⁶

MnO: Oelsen and Maetz found that even 12% MnO in the upper layer does not alter the miscibility gap. In other words, MnO does not change the shape, size or extent of the gap. Without incurring any serious error, it is possible to write $\text{FeO} + \text{MnO}$ instead of FeO in the ternary phase diagram.

As with FeO , MnO also is partitioned between the upper and lower layers. This should affect the FeO -content and, therefore, the

oxidising power of both the slag layers. It is natural to expect that the presence of MnO will affect the dephosphorising action of FeO in the upper phosphate layer. However, the ratios P_2O_5 -lower/ P_2O_5 -upper for various FeO-contents of upper layer in MnO-free and MnO-containing slags do not show any influence of MnO. Therefore, it can be assumed that FeO and not MnO determines the dephosphorisation. MnO acts merely as a diluent.⁵⁵

Magnesia⁵⁶ : It enters as an impurity in Thomas slag from the dolomite lining of the converter. It is not very soluble in such slags and the saturation-content seems, for 16-20% Fe in the slag, to be 4-6% ; more of MgO in the slag remains undissolved. It lowers the solubility and the activity of lime and, therefore, retards phosphorus and sulphur removal.

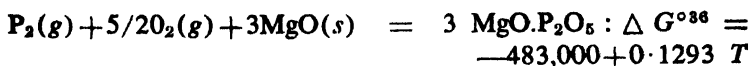
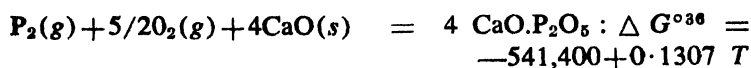
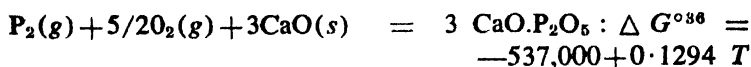
Alumina⁵⁶ : Its amount is generally within 1% in the usual Thomas slag. It liquefies such a slag earlier and, therefore, dephosphorisation starts earlier. With increasing alumina more manganese is oxidised to slag, desulphurisation is worsened. Alumina probably lowers the activity of lime and increases the activity of FeO.

Titania⁵⁶ : It is generally almost absent. It is a good liquefying agent for lime. Manganese oxidation is not affected by it and desulphurisation only to a slight extent.

Sodium Oxide⁵³ : It increases the basicity of the slag. Presence of Na_2O enlarges the miscibility gap. It is used for 'fine' dephosphorisation of Thomas iron.

Temperature⁵³ : Lower temperature enlarges the miscibility gap to a little extent but the saturation-content of lime in the slag is lowered by a greater amount. Lower temperature helps dephosphorisation.

Fe—P—O—CaO



We have mentioned in the previous two sections that removal of phosphorus from metal to slag is facilitated by low temperature, highly oxidising slag or oxidised metal and by high basicity. These qualitative criteria for dephosphorisation are known to all basic steel melters but a quantitative correlation in regard to slag-metal equilibria could not be satisfactorily obtained. This has been rendered more difficult because of the large numbers and different nature of slag constituents. Because of mutual interactions of the various constituents it is not possible to use simple concentration terms in the equilibrium equation. Activity terms must be used and these terms are difficult to evaluate in complex slags.

The initial product of oxidation of phosphorus in iron is gaseous P_2O_5 and little [P] is lost to the gaseous phase. A formation of stable phosphate is necessary for phosphorus removal. Iron phosphate slag can dephosphorise only to a limited extent but lime does so extensively, forming calcium tri- or tetra-phosphate.

For the purpose of calculations, the formation of either the tri- or the tetra-phosphate may be assumed, since according to Richardson⁵⁷ their free energies of formation do not differ considerably from each other. We would, therefore, consider the formation of tetra-phosphate for the present :



the equilibrium constant of the reaction being

$$K = \frac{(4 CaO.P_2O_5).[Fe]^5}{[P]^2.(FeO)^5.(CaO)^4} \quad 3.31$$

Obviously the concentrations in the equations cannot be the analytically determined values. CaO and FeO are 'free' concentrations as defined by Schenck²³. Since it is assumed that entire $\leq P_2O_5$ is combined as tetra-phosphate, and therefore $\leq P_2O_5$ is proportional to the phosphate and further, since in steelmaking processes the concentration of iron does not vary appreciably, we can include the iron concentration and the proportionality factor of $\leq P_2O_5$ in the equilibrium constant :

Therefore, Eq. 3.31 becomes,

$$K' = \frac{(\leq P_2O_5)}{[P]^2.(FeO)^5.(CaO)^4} \quad 3.32$$

$$\text{Or, } \frac{(\leq \text{P}_2\text{O}_5)}{[\text{P}]^2} = K' \cdot (\text{FeO}')^5 \cdot (\text{CaO}')^4 \quad 3.33$$

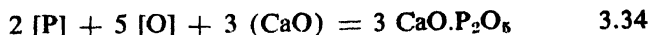
where FeO' and CaO' are the respective 'free' concentrations.

It is clear from Eq. 3.33 that dephosphorisation increases with increasing FeO and CaO. But such increases, at least for Thomas process, are limited by lime-saturation of the slag. FeO can only be increased provided sufficient lime is available. Otherwise the danger exists that with rising FeO, the region of the 'miscibility gap' will be reached beyond which it may be futile to increase the FeO as it will not aid dephosphorisation any further, rather a rephosphorisation may take place. In case of basic open-hearth process as well, at any given temperature and lime-silica ratio (i.e. basicity ratio) there is a limit to dephosphorisation with increasing FeO and for a given FeO there is no dephosphorisation beyond a certain basicity of the slag.

The knowledge of equilibrium relations is necessary to find the extent and mechanism of dephosphorisation as well as the conditions under which rephosphorisation, i.e. migration of phosphorus from slag to metal can take place. For the calculation of the equilibrium constant, we should take the activities of the slag constituents into consideration because of the mutual interaction of the constituents as well as the influence of impurities present in the slag. The calculation of the activities in steelmaking slags is, however, difficult and methods have been devised to circumvent the use of activity terms but these have only limited applicability.

Thomas slag

Fischer and Vom Ende⁵⁸ investigated the phosphorus equilibrium in lime crucibles free from impurities. Since iron oxide in the slag is related to oxygen-content of the melt it is admissible to use [O] in place of FeO in the calculation of the equilibrium constant. They assumed the following reactions to take place in their experiments in CaO-crucibles :



$$\text{and } K = \frac{(3 \text{CaO} \cdot \text{P}_2\text{O}_5)}{[\text{P}]^2 \cdot [\text{O}]^5 \cdot (\text{CaO}')^3} \quad 3.35$$

Here $[P]$ and $[O]$ are in wt.% and $3 \text{ CaO} \cdot \text{P}_2\text{O}_5$ and CaO' are in mol fractions where CaO' is the lime remaining after combination with P_2O_5 as $3 \text{ CaO} \cdot \text{P}_2\text{O}_5$. They assumed after an extensive examination of the slag under microscope that it contained $3 \text{ CaO} \cdot \text{P}_2\text{O}_5$ rather than $4 \text{ CaO} \cdot \text{P}_2\text{O}_5$. On plotting $\log K$ against $1/T$ they found that K decreased with increasing temperature, i.e. phosphorus content in metal increased. Since, however, the experimental points distribute themselves in a way that shows that K -value is dependent on P_2O_5 of the slag, the law of mass action based on concentration cannot obviously be applied and the activities of the slag constituents must be substituted in Eq. 3.35. Since the liquid $\text{FeO}-\text{CaO}-\text{P}_2\text{O}_5$ slag is contained in lime-crucible, the activities of CaO and $3 \text{ CaO} \cdot \text{P}_2\text{O}_5$ may be assumed to be constant and since $a_{[P]}$ and $a_{[O]}$ are proportional to their wt.%,

$$K' = 1/([P]^2 \cdot [O]^3) \quad 3.36$$

$$\text{or } \log [O] = -2/5 \log [P] - 1/5 \log K' \quad 3.37$$

If $\log [O]$ is drawn against $\log [P]$ then a straight line should be expected whose inclination will be -0.4 . This was found to be true. When $\log K'$ is plotted with $1/T$ a straight line of the following equation is obtained,

$$\log K' = 53,000/T - 19.4 \quad 3.38$$

Eqs. 3.37 and 3.38 also furnish the extent of deoxidation of steel with phosphorus under lime-saturated iron oxide slags. Oxygen decreases with increasing phosphorus. At $1,650^\circ\text{C}$ when $[P] = 0.03\%$, the $[O]$ -content is 0.12% . At $[P] = 1\%$, $[O] = 0.025\%$.

The extent of dephosphorisation in lime-saturated iron oxide slag can be seen from the relation of P_2O_5 and $[P]$ in Fig. 3.29. The equilibrium was reached from metal side by the oxidation of $[P]$ and from slag side by the reduction of P_2O_5 . The figure shows that the end $[P]$ increases with increasing temperature, viz. with $\text{P}_2\text{O}_5 = 16\%$ between $1,530^\circ$ — $1,570^\circ\text{C}$, $[P] = 0.01\%$ and for the same P_2O_5 between $1,620^\circ$ — $1,700^\circ\text{C}$, $[P] = 0.03\%$. For any given temperature, $[P]$ remains almost the same between about 5% and $30\% - \text{P}_2\text{O}_5$. Above 30% and below $5\% \text{ P}_2\text{O}_5$ the increase in $[P]$ is very steep. This must be due to the tendency of $\text{CaO}-$

$\text{FeO-P}_2\text{O}_5$ slag, between the said amounts of P_2O_5 , to separate into two layers. But the investigators could not actually find any such separation. Fig. 3.29 also shows the feasible limit of dephosphorisation in the Thomas process where, at the end of the blow,

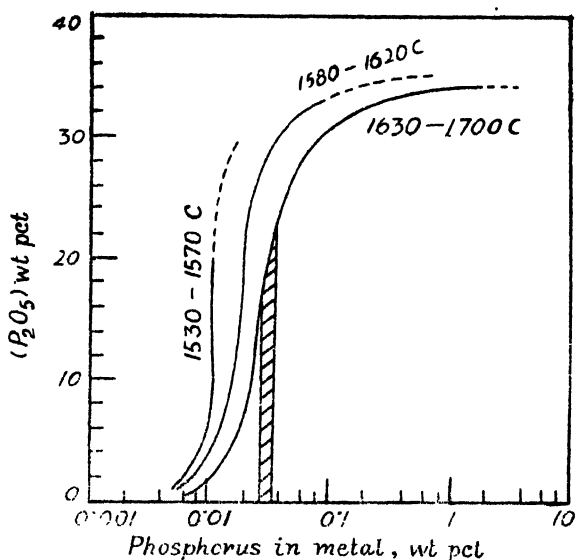


Fig. 3.29—The phosphorus distribution between liquid iron and lime saturated FeO-slag for temperatures 1,530-1,700°C. The range of P_2O_5 contents of the common Thomas slags and phosphorus contents of metal are also shown by the shaded area. (K. G. Speith & H. V. Ende, *Stahl und Eisen*, 72, 1952, 1938).

temperatures of around 1,650°C are usual. Under an almost pure $\text{FeO-P}_2\text{O}_5\text{-CaO}$ slag, $[\text{P}] \sim 0.03\%$ can be reached with P_2O_5 in slag in the range of actual basic practice. $[\text{P}] = 0.04\text{--}0.05\%$ is frequently attained. At much lower temperatures, $[\text{P}]$ as low as 0.01% cannot be ruled out. Lower phosphorus contents can also be achieved by 'fine dephosphorisation' (cf. chapter viii).

It may be questioned whether such equilibrium experiments under pure slags are of any use in the Thomas, let alone the basic open-hearth processes. It is true that in basic open-hearth the slag contains large amount of silica, very low P_2O_5 and also fair amounts of other impurities like MgO , Al_2O_3 , CaF_2 , Fe_2O_3 , etc. and, therefore, experiments like the above investigations are of no use. But they are helpful for understanding the Thomas

process because an impurity like silica, though it narrows down the 'miscibility gap' on the $\text{FeO-P}_2\text{O}_5$ side of $\text{FeO-P}_2\text{O}_5\text{-CaO}$ system considerably, does not do so on the CaO-FeO side. Since the composition of Thomas slag lies on this side, it makes it possible to compare this process with the experiments in the laboratory with pure $\text{FeO-P}_2\text{O}_5\text{-CaO}$ slags.

In practical steelmaking the end oxygen-content is of extreme importance in view of the quality of metal and its subsequent behaviour during mechanical treatment or in service. Fischer and Vom Ende⁵⁸ made extensive investigations on [P] and [O] equilibrium under lime-saturated $\text{FeO-P}_2\text{O}_5\text{-CaO}$ slags. Subsequently other workers followed^{47-49,59}. Recently Knüppel and Oeters⁵⁵ directed their efforts towards the same object.

In liquid iron under a lime-saturated phosphate slag, the equilibrium [P]- and [O]-contents are determined by the slag composition. At any given temperature, the slag composition can be clearly depicted by the concentration of only one component, i.e. either total iron or phosphorus pentoxide since the composition follows the lime-saturation line which runs almost parallel to the base of the ternary phase diagram (Fig. 3.25) and, therefore, shows more or less constant amount of lime in the entire phase system. However, the Thomas steel workers generally use total iron ($\leq \text{Fe}$) to indicate the slag composition. Fig. 3.30 has been drawn with [P] and [O] contents as functions of ($\leq \text{Fe}$) for three different temperatures. As can be seen, [O] increases rapidly at first and later almost imperceptibly with increasing ($\leq \text{Fe}$) which corroborates the non-ideal behaviour of Thomas slag. The [P]-content which depends on the state of oxidation of metal and slag also behaves in the same manner and only when ($\leq \text{Fe}$) is very high ($\sim 45\%$), i.e. when phosphorus in slag is almost nil does [P] fall and approach zero.

That [P] and [O] should behave in the way as said above is understandable because both are controlled by a_{FeO} and, therefore, by ($\leq \text{Fe}$) of slag. ($\leq \text{Fe}$) and a_{FeO} are interrelated. According to Fischer and Vom Ende, a plot of a_{FeO} against ($\leq \text{Fe}$) shows that below 20% (Fe) the a_{FeO} falls rapidly, (therefore [P] increases and [O] decreases steeply); between 20-50% ($\leq \text{Fe}$) the a_{FeO} remains almost constant (therefore [P] and [O] both remain more or less constant).

The influence of temperature on the equilibrium [P] and [O] contents is also shown in Fig. 3.30⁵⁵. Both these elements show higher values with increasing temperature. The temperature-dependence of [O] under lime-saturated phosphate slag is, however,

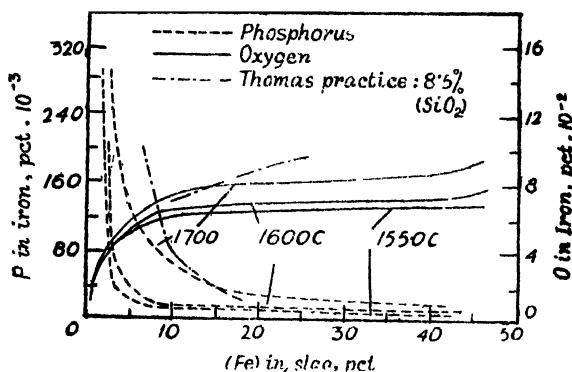


Fig. 3.30—The influence of temperature on the equilibrium relations of phosphorus & oxygen in metal and iron content of slag. (H. Knüppel & F. Oeters, *Stahl und Eisen*, 81, 1961, 1437-49). The values for Thomas practice are also shown.

smaller than under pure (FeO). While [O] under a phosphate slag with 15% (Fe) and between 1,550°C and 1,700°C increases from 0.062% to 0.073%, i.e. by a factor 1.2, it increases in case with pure (FeO) under the same conditions (Eq. 3.6) from 0.20 to 0.30% [O], i.e. by a factor 1.5. The smaller increase of [O] under the phosphate slag indicates that a_{FeO} in such slags decreases with increasing temperature. The [P] and [O] curves for 1,550° & 1,600°C, with more than 10-15% ($\leq \text{Fe}$), are more or less horizontal, i.e. they change very little whereas those for 1,700°C continue to fall and rise respectively with increasing ($\leq \text{Fe}$).

The above discussions are concerned with pure $\text{FeO-P}_2\text{O}_5\text{-CaO}$ system. Thomas slags, however, contain impurities of SiO_2 , MnO and small amounts of Al_2O_3 , MgO , etc. Knüppel and Oeters⁵⁵ have found that as long as the slag is lime-saturated, up to 8% SiO_2 and 4% MnO have no specific influence on [P] and [O] contents and these do not deviate from Fig. 3.30. In actual Thomas practice the equilibrium is not attained and SiO_2 delays dephosphorisation and increases end-oxygen in steel. (cf. Fig. 3.30).

Basic Open-hearth slag

Thomas slag is very different from basic open-hearth slag. The former contains low SiO_2 and high P_2O_5 whereas the latter contains considerable amount of SiO_2 and only 1-5% of P_2O_5 . In such a slag there is no possibility of any tendency towards immiscibility, first because of low P_2O_5 and secondly because the 'miscibility gap' becomes non-existent above about 15% SiO_2 .

The phosphorus equilibrium in basic open-hearth cannot be calculated easily. The slag here contains several constituents which render the activities of the reacting species difficult to evaluate. The constitution of such slags is not fully known and without a satisfactory slag model the application of mass law is bound to lead to erroneous results.

Schackmann and Krings⁶⁰ and Maurer and Bischof⁶¹ suggest that the deviations from equilibrium constants of phosphorus reaction can be much narrowed down if $[\text{P}]$ and not $[\text{P}]^2$ is substituted in Eq. 3.31. Schenck and Riess⁶² have also adopted the same procedure in their equation for dephosphorisation in open-hearth. The use of their equation has been dealt with on p. 260.

Winkler and Chipman⁶³ studied the phosphorus equilibrium extensively with laboratory melts using radioactive phosphorus to ascertain the attainment of equilibrium.

In terms of activities the phosphorus removal Eq. 3.31 can be written as :

$$K' = \frac{(a_{\text{Ca}_3\text{P}_2\text{O}_8}) \cdot (a_{[\text{Fe}]})^5}{(a_{[\text{P}]})^2 \cdot (a_{\text{FeO}})^5 \cdot (a_{\text{CaO}})^4} \quad 3.39$$

In view of the large amount of iron, a_{Fe} may be considered equivalent to unity; phosphorus being very low, $a_{[\text{P}]}$ can be taken as proportional to wt.%; and since at any temperature a_{FeO} is proportional to % $[\text{O}]$, a_{FeO} can be substituted by actual oxygen concentration, the proportionality factor of the above being included in the equilibrium constant value. Again, assuming activities of the phosphate and lime to be equivalent to the mol fraction of 4 $\text{CaO} \cdot \text{P}_2\text{O}_5$ and available lime CaO' , Winkler and Chipman set out to find the slag constitution which would furnish 'non-variable' equilibrium constant under the above assumptions. The equilibrium constant is given as^{63,64},

$$Kp = \frac{(N_{4\text{CaO.P}_2\text{O}_5})}{\% [\text{P}]^2 \cdot \% [\text{O}]^5 \cdot (N_{\text{CaO}}')^4} \quad 3.40$$

the dephosphorisation equation being,



$$\log Kp = 71,670/T - 28.73 \quad 3.42$$

In order that Eq. 3.40 may be useful for practical purposes, % [O] has been replaced in Eq. 3.43 by N_{FeO} , the necessary correction for oxygen distribution having been made :

$$Kp' = \frac{N_{4\text{CaO.P}_2\text{O}_5}}{\% [\text{P}]^2 \cdot (N_{\text{FeO}})^5 \cdot (N_{\text{CaO}}')^4} \quad 3.43$$

$$\log Kp' = 40,070/T - 15.06 \quad 3.44$$

It has been found that $\log Kp'$, determined by laboratory experiments, agree well with the values computed from actual open-hearth data.

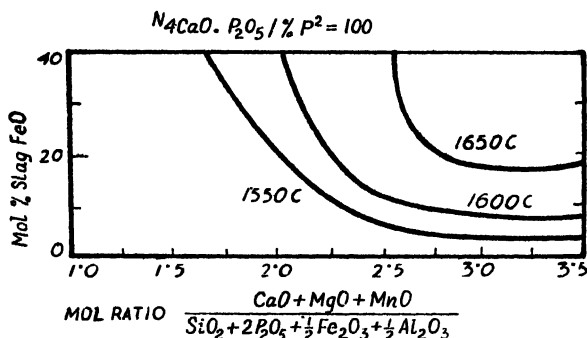


Fig. 3.31—The influence of temperature and slag composition on the lines of constant dephosphorisation ratio. (T. B. Winkler & J. Chipman, Trans. AIME, 167, 1946, 111, 33).

From the above considerations Derge and Tencnbaum⁶⁴ have put forward Fig. 8.2 which is very useful for open-hearth melters. The figure shows the influence of (FeO) and basicity of slags on residual phosphorus of metal. The influence of temperature is

shown in Fig. 3.31⁶³. It is clear that to maintain the same dephosphorisation potential, it is necessary to increase both basicity and FeO content of slag as the temperature increases. The beneficial effect of lower temperature is apparent.

Balajiva *et al*⁶⁵⁻⁶⁷ also investigated the phosphorus distribution extensively at 1,535°, 1,585° and 1,635°C. They depict the equilibrium constant as

$$K = \% (P_2O_5) / (\% (\leq FeO)^5 \cdot \% [P]^2)$$

$$\text{and } \log K = 10.78 \log \% (\leq CaO) - n$$

where FeO = total Fe-content converted to FeO

$$n = 20.08, 20.41, 20.83 \text{ at } 1,535^\circ, 1,585^\circ, 1,635^\circ\text{C} \text{ respectively.}$$

They concluded that for each slag basicity (CaO/SiO₂) there is an optimum (FeO) which when exceeded decreases the $\% (P_2O_5) / \% [P]$ ratio, i.e. affects the dephosphorisation adversely.

It is difficult indeed to form a coherent idea regarding the mechanism of dephosphorisation of iron under basic open-hearth slag. The investigators have used their own slag models in order to obtain a reasonable equilibrium constant. The only answer to the problem is to use the activity values which has been described on p. 267.

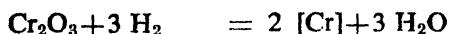
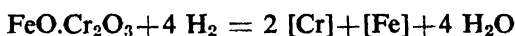
The problem can also be circumvented by the use of ionic theory of slags. The application of this theory is, however, still in its infancy and, therefore, its discussion has not been attempted here. The reader may refer to the works of Herasymenko and Speight^{68,69} Flood and Grojtheim⁷⁰.



$$\begin{array}{lll} 4/3 Cr + O_2 & = 2/3 Cr_2O_3 & : \quad \Delta G^\circ (298^\circ - 1,868^\circ K) \\ & & = -178,500 + 41.40 T \\ \text{m.p. Cr} & = 2,070^\circ K & : \quad \Delta G^\circ (1,868^\circ - 2,500^\circ K) \\ & & = -183,740 + 44.21 T \end{array}$$

Chromium is a costly metal and its elimination in the slag during steelmaking is a substantial loss. It is susceptible to oxidation and its affinity for oxygen is intermediate between that of manganese and vanadium. Steel containing significant amounts of Cr shows inclusions of two oxides, viz. Chromic oxide (Cr_2O_3) and chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$). They are moderately stable at steelmaking temperatures but less so than the oxides of Si or Al and, therefore, Cr cannot be classed as a good deoxidiser. Its affinity for oxygen decreases with increase in temperature and advantage of this phenomenon is taken for the retention of the element in the bath during the production of chromium-steels of heat-and corrosion-resisting and austenitic stainless varieties in electric furnaces.

The study of equilibrium relations between chromium and oxygen dissolved in steel depends on the type or variety of the oxide formed. The above-mentioned two oxides are formed from low- and high-chromium steel. Chen and Chipman⁷¹ carried on equilibrium experiments with molten iron in chromite and chromic oxide crucibles under an atmosphere of $\text{H}_2/\text{H}_2\text{O}$ mixtures. Plotting $\log [\text{Cr}]$ against $\log \text{H}_2\text{O}/\text{H}_2$, they found two straight lines intersecting at 5.5 [Cr]. The reactions involved in the two types of crucibles are :



It is suggested that about 5-7% Cr in iron is a critical content, below which the [Cr] and [O] equilibrium gives rise to stable brown chromite phase while above this amount the stable phase is green chromic oxide. Chen and Chipman conclude that at 1,595°C the stable phase is Cr_2O_3 with Fe-Cr alloys containing more than 5.5% Cr. The free energy relation is :

$$2[\text{Cr}] + 3[\text{O}] = \text{Cr}_2\text{O}_3 (s) : \Delta G^\circ = -194,750 + 83 \cdot 12 T \quad 3.45$$

The effect of temperature on the equilibrium is very great. The oxygen-content increases, that is the deoxidising power of Cr decreases, with increasing temperature. According to calculated values,⁷¹ the [O]-contents of 10% Cr alloy are 0.017% at 1,540°C; 0.041% at 1,650°C; 0.086% at 1,760°C.

Chromium possesses a peculiar influence on oxygen in liquid iron. Its deoxidising action increases up to 4.5% Cr. After

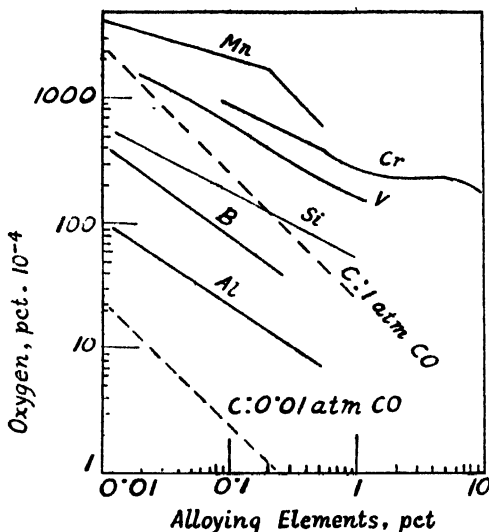


Fig. 3.32 (a)—Relation between oxygen-contents and alloying elements in molten steel at 1,600°C.

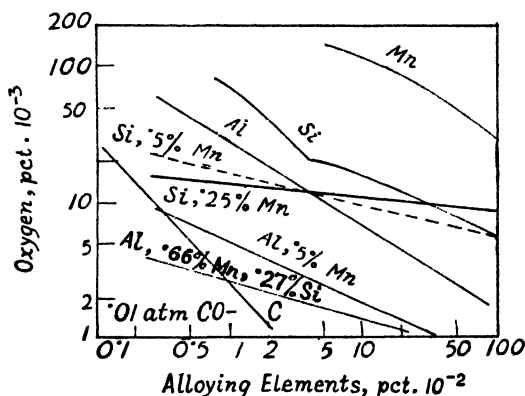


Fig. 3.32 (b) Deoxidising power of silicon, manganese and aluminium singly and together. The action of carbon at $p_{CO} = 0.01$ atm is also shown.

exerting the maximum effect at this concentration, the oxygen content no longer diminishes, and if at all, rather slowly because of the marked lowering of the oxygen activity in iron at higher Cr-concentrations. At this stage, probably because of formation

of chromic oxide from chromite, there is a sudden steep decline in the slope of oxygen-activity, whereas the oxygen-content begins to rise slowly. The deoxidation curve of Cr is shown in Fig. 3.32a.

Fe—Cr—O—C

This system is important from the point of view of decarburisation of stainless steel. As we know, the resistance of chrome-nickel stainless steel to corrosion increases as the carbon content decreases. The so-called 18/8 austenitic steels containing carbon of the order 0.03%, are corrosion resistant. The difficulty of producing such steels lies in the fact that at steelmaking temperatures chromium is oxidised in preference to carbon as shown by the evolution of strong brown fumes, resulting in serious loss of the valuable metal in the slag. The high chromium slag creates operational difficulties also, since such slags are solid at these temperatures. But, in the neighbourhood of 1,800°C, chromium and carbon oxidation reactions are almost reversed. This very high temperature can be reached rapidly by the injection of oxygen at the slag-metal interface of the molten bath.

According to Hilty,^{73,74} the following reaction takes place :



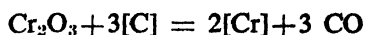
The plot of the logarithms of % [C] and % [Cr] gives a slope of unity whereby it can be assumed that % [Cr]/% [C] = constant. The equilibrium constant of the reaction, when $p_{\text{CO}} = 1$ atm. and $a_{\text{CrO}} = 1$ in the slag, is given by :

$$\log K = \log \% [\text{Cr}] / \% [\text{C}] = -13,800/T + 8.76$$

The Cr/C ratio calculated from the above equation is

	1,627°C	1,727°C	1,827°C
% [Cr]/% [C] from equation	33	72	158
In actual experiment			
for 0.1% residual carbon		60	150
“ “		60	153

According to Richardson and Dennis,⁷⁵ the decarburisation takes place thus :



Activity of carbon is influenced by the concentration of $[\text{Cr}]$ and $[\text{C}]$ and Hilty's straight line must be due to the fact that the activity co-efficient of carbon is lowered by Cr in such a way that

$$\% [\text{Cr}] / \% [\text{C}] = \text{constant}$$

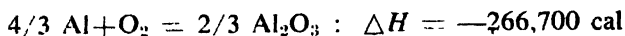
If it is assumed that ideal behaviour of Cr is not affected by low C-content, $p_{\text{CO}} = 1$ atm. and $a_{\text{Cr}_2\text{O}_3} = 1$ in solid chromic oxide slag, then ^{72b}

$$K = \% [\text{Cr}]^2 / a^3 [\text{C}] \text{ and } \log K = -33,620/T + 21.9$$

Carbon activities can be calculated from the data of Richardson and Dennis.

Fe—Al—O

The free energies of the oxidation reactions of aluminium are :



Melting points : Al = 931.7°K ; $\text{Al}_2\text{O}_3 = 2,303^\circ\text{K}$

$$\Delta G^\circ (298^\circ - 930^\circ\text{K}) = -256,600 + 43.3 T \pm 10,000 \text{ cal}$$

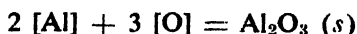
$$\Delta G^\circ (930^\circ - 2,318^\circ\text{K}) = -257,500 + 44.3 T \pm 10,000 \text{ cal}$$

$$\Delta G^\circ (2,318^\circ - 2,330^\circ\text{K}) = -240,400 + 36.8 T \pm 10,000 \text{ cal}$$

$$\Delta G^\circ (2,330^\circ - 2,500^\circ\text{K}) = -321,600 + 71.8 T \pm 10,000 \text{ cal}$$

In view of the great affinity of oxygen for aluminium the latter

element is used extensively for deoxidation of steel. The reaction is given by :



Assuming the activity of alumina to be unity, the equilibrium constant is

$$K = \% [\text{Al}]^2 \cdot \% [\text{O}]^3, \quad 3.46$$

the temperature function being,⁷⁶ $\log K = -64,000/T + 20.48$

$$K (1,600^\circ\text{C}) = 2.10^{-14}$$

Higher values have been given by other investigators.⁷⁷

The relation between Al and O is shown in Fig. 3.32 from where it is clear that aluminium is by far the strongest deoxidiser surpassed by carbon only at a very low partial pressure of carbon monoxide ($p_{\text{CO}} \sim 0.01$ atm).

The products of oxidation are insoluble in steel and may separate out or remain as non-metallic inclusions in solidified metal, depending upon circumstances (cf. p. 367). In the case of aluminium deoxidation it is surmised^{77b} that at $1,600^\circ\text{C}$ and $[\text{Al}] > 0.1\%$ mixed inclusions of $\text{FeO} \cdot \text{Al}_2\text{O}_3$ (hercynite) and Al_2O_3 are formed; with $[\text{Al}] < 0.1\%$, the mixture contains FeO and $\text{FeO} \cdot \text{Al}_2\text{O}_3$. Both alumina and hercynite are solid at steelmaking temperatures.

The $\text{FeO}-\text{Al}_2\text{O}_3$ phase diagram, (Fig. 3.40c)⁷⁸, however, shows the existence of hercynite and $3 \text{FeO} \cdot \text{Al}_2\text{O}_3$. The latter has not yet been identified in the inclusions.

Fe—Mn—Al—O

The deoxidising power of aluminium is considerably increased in the presence of manganese. This has been shown by Hilty and Crafts⁷⁷ in their experiments with liquid iron containing \sim

0.45% [Mn] to which progressively increasing amounts of aluminium were added. (*cf.* Fig. 3.32(*b*)).

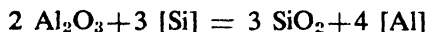
The deoxidation products evidently belong to the FeO—MnO—Al₂O₃ system.⁷⁹ In the phase diagram, there is a field of primary crystallisation of spinel (FeO.MnO). Al₂O₃. Therefore, the constituents of the inclusions can only be a mixture of alumina and spinel and possibly, a FeO.MnO solid solution. The diagram also shows that inclusions containing more than 30% alumina will be solid at 1,550°C.

The decreasing solubility of oxygen with increasing Mn—content may probably be due to progressive replacement of FeO by MnO in the spinel (FeO.MnO). Al₂O₃, thereby decreasing the activity of FeO.

Oelsen and Heynert⁸⁰ have investigated into the amount of oxygen and manganese in liquid iron that would give (in the presence of Al) liquid MnO—Al₂O₃ solution. Curve III in Fig. 11.3 shows that lower the [Mn], the higher must be [O] for obtaining liquid aluminate. Since carbon decreases the activity of oxygen the relative oxygen contents will be higher in presence of carbon as shown by Curve III *a*.

Fe—Si—Al—O

In contrast to manganese, there is at present no evidence that silicon affects the deoxidising power of aluminium. The above system has been investigated by Geller and Dicke⁸¹ who assumed the presence of an alumina-saturated slag :



$$K = (\% [\text{Al}])^4 \cdot (\% \text{ SiO}_2)^3 / (\% [\text{Si}])^3$$

$$\text{At } 1,600^\circ\text{C}, K = 4.10^{-5}$$

The inclusions will naturally belong to FeO—SiO₂—Al₂O₃ system.⁸² The presence of four compounds is indicated:^{82 d} 2 FeO.SiO₂ (fayalite), 3Al₂O₃.2SiO₂ (mullite), FeO.Al₂O₃ (hercynite), 2FeO.2Al₂O₃.5SiO₂ (iron cordierite). If Al is

added to a Si-deoxidised steel containing solid silica, the primary phase in inclusions will be mullite when $\text{Al}_2\text{O}_3 < 55\%$ and corundum when $\text{Al}_2\text{O}_3 > 55\%$. If the primary inclusions are liquid iron silicates, a variety of inclusions will result depending upon the amount of alumina formed and the composition of iron silicate. With $\text{Al}_2\text{O}_3 < 50\%$, glassy silicates are possible.⁸³

Fe—Mn—Si—Al—O

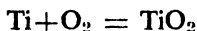
The presence of silicon and manganese increases the deoxidising power of aluminium. Curve II Fig. 11.3 shows [O] and [Mn] contents in steel for the production of a liquid slag, an iron-manganese-silicate with about 20% alumina. (See also Fig. 3.32(b)).

The inclusions formed belong to $\text{FeO—MnO—SiO}_2\text{—Al}_2\text{O}_3$ system. As is evident, there are many possibilities of combination of the constituents. Depending upon the Al_2O_3 -content, the inclusions may be glassy or crystalline. The possible compounds are:^{83,84}

$\text{MnO} \cdot \text{Al}_2\text{O}_3$; $2\text{MnO} \cdot \text{SiO}_2$ and $\text{MnO} \cdot \text{SiO}_2$; $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$; $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. The last two form low melting ternary eutectics with the other constituents.

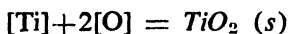
Fe—Ti—O

The data regarding Ti—O are :



$$\Delta G^\circ (298^\circ\text{—}2,080^\circ\text{K}) = -217,500 + 41 \cdot 4 T \pm 10,000 \text{ cal}$$

Titanium has a great affinity for oxygen and its deoxidising power in liquid iron is given by⁸⁵ :



$$K = \%[\text{Ti}] \cdot \%[\text{O}]^2$$

$$\log K = -33,830/T + 11 \cdot 8$$

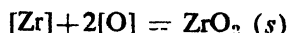
Fe—Zr—O

The data regarding Zr—O are :



$$\Delta G^\circ = -256,000 + 44.0 T$$

It is one of the strongest deoxidising agents as is evident from the following :⁷⁶



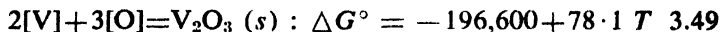
$$K = \%[\text{Zr}] \cdot \%[\text{O}]^2$$

$$\log K = -41,340/T + 12.07 \quad 3.48$$

Fe—V—O⁷⁶

When liquid ferro-vanadium is equilibrated with $\text{H}_2/\text{H}_2\text{O}$, the plot of oxygen in metal and the gas ratio shows a break as in the case of chromium but at a much lower V-content, about 0.16%. The oxides identified above and below this concentration are V_2O_3 and a spinel $\text{FeO} \cdot \text{V}_2\text{O}_3$ respectively.

As with chromium, the activity co-efficient of oxygen is decreased by vanadium and the effect of 0.1% is equivalent to that of 0.5% Cr. The influence of carbon is of the same order as V. The free energy of V-deoxidation is given by :



$$K (1,600^\circ\text{C}) = 1.75 \cdot 10^{-6}$$

The deoxidation curve is shown in Fig. 3.32.

FeB—O

The deoxidation product of boron as calculated by Chipman⁷⁶ from the experimental results of Derge⁸⁶ is given by :

$$\%[\text{B}]^2 \cdot \%[\text{O}]^3 = 4.10 \cdot 10^{-9} \text{ at } 1,600^\circ\text{C} \quad 3.50$$

Others⁸⁷ have given values which are somewhat higher than the above. The deoxidation curve is shown in Fig. 3.32.

Fe—H

Defects like flakes and hair-line cracks in cast steel have been attributed to the presence of hydrogen. This is also evident from its solubility in iron (Fig. 3.33¹²) which decreases suddenly at the freezing point of iron. It again increases from δ - to γ iron and decreases further on from γ to α -iron. Since hydrogen is more soluble in the liquid than in the solid iron, the gas comes out of the solid phase as the liquid freezes and progressively concentrates in the rest metallic melt. This continues until the solubility limit is reached, when the gas starts forming bubbles resulting possibly in the so-called 'hydrogen wilderness' or 'blow holes'.

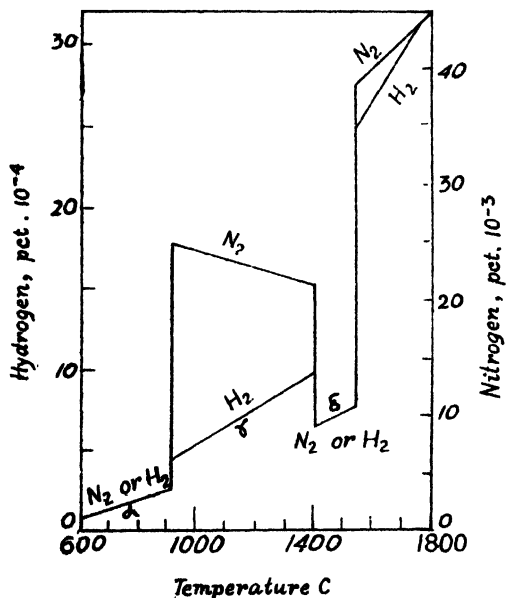


Fig. 3.33—The influence of temperature on the solubility of hydrogen & nitrogen in iron at one atmosphere pressure of the gases. (J. Chipman, Basic Openhearth Steelmaking, AIME, Copyright 1951).

The absorption of hydrogen in steel is rapid when exposed to an atmosphere containing the gas, and the equilibrium is easily

established between the gas in the atmosphere and that in steel. The evolution of the gas from steel under favourable conditions is also more or less rapid. The amount of the gas in iron can be calculated from Sievert's law,

$$1/2 \text{ H}_2 = [\text{H}] : K = \% [\text{H}] / (p_{\text{H}_2})^{1/2} \quad 3.51$$

where p_{H_2} is in atmospheres and $\% [\text{H}]$ in wt. per cent. The temperature functions of K for pure iron are given by²³ :

$$\begin{aligned} K (\alpha - \text{Fe}) &= 48 \cdot 10^{-8} t^{\circ}\text{C} - 17 \cdot 2 \cdot 10^{-5} \\ K (\gamma - \text{Fe}) &= 88 \cdot 10^{-8} t^{\circ}\text{C} - 37 \cdot 2 \cdot 10^{-5} \\ K (\delta - \text{Fe}) &= 60 \cdot 10^{-8} t^{\circ}\text{C} - 30 \cdot 0 \cdot 10^{-5} \\ K (\text{liq} - \text{Fe}) &= 275 \cdot 10^{-8} t^{\circ}\text{C} - 175 \cdot 5 \cdot 10^{-5} \text{ (approx.)} \end{aligned} \quad 3.52$$

For Eq. 3.51, $\Delta G^{\circ} = 7,640 + 7 \cdot 68 T$ (hypothetical 1% solution).¹² More recent data is ¹²⁴, $\log K = 1,670/T + 2 \cdot 32$.

It is clear from Eqs. 3.51 & 3.52, the evolution pressure in general increases during cooling and in the α -field where the solubility is very low, the evolution pressure may be tremendous at low temperatures.

The magnitude of the evolution pressure of hydrogen in steel has been calculated for various temperatures and hydrogen contents 0.001—0.003% by Schenck and Luckemeyer-Hasse.²³ The results are reproduced in Fig. 3.34. It is clear from the figure that the evolution pressure p_{H_2} can exceed the $P_{a(\text{liq})}$ (hydrostatic pressure of liquid column) in the solidification range 1400°—1480°C. Here, if the hydrogen content exceeds 0.0010% it is possible that gas may evolve resulting in hydrogen-wilderness.

At low temperatures p_{H_2} can attain considerable magnitude and might exceed the tensile strength of steel, as is seen from the shaded area in the figure. The p_{H_2} -curve of $[\text{H}] = 0.0010\%$ meets the tensile strength curve near about 400°C. It is quite possible that high evolution pressure inside a steel casting would produce great internal stress which may affect the mechanical properties of the material if the gas fails to escape from the interior.

It is not difficult for hydrogen to diffuse out from solid castings because of its small atomic size. The diffusion increases with tem-

perature. Therefore, high quality steel intended to be forged is normally annealed for a long period (2 to 3 weeks for very large

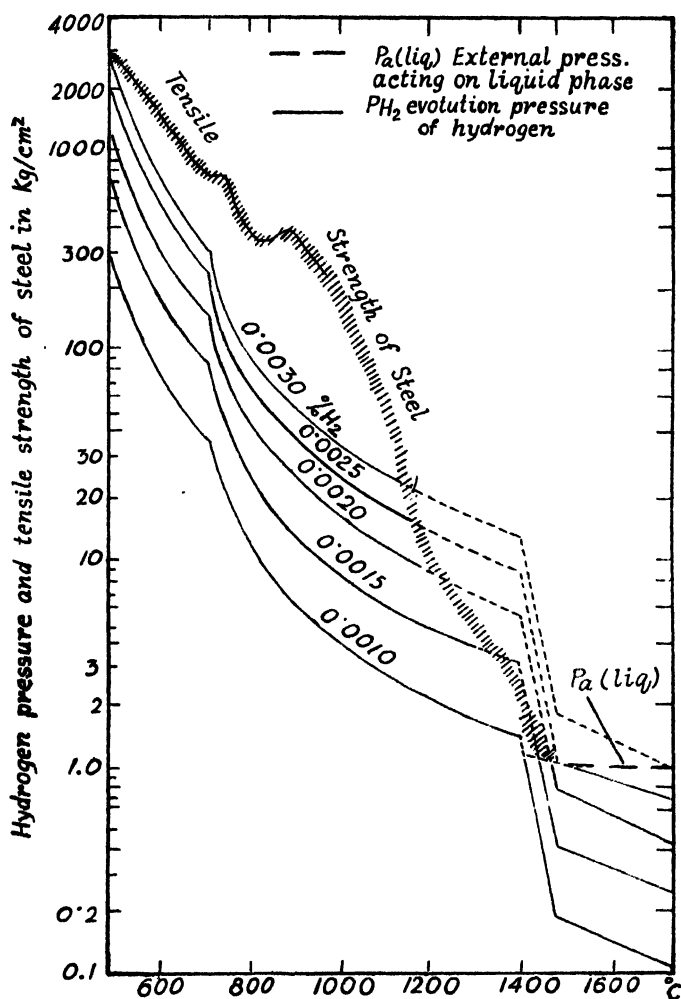
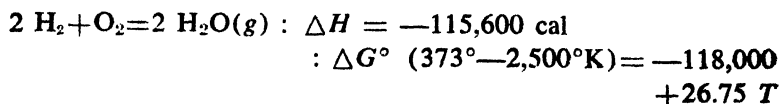


Fig. 3.34—Evolution pressure of hydrogen in steel. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

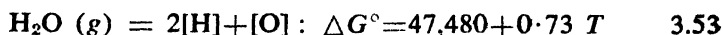
size) for driving out the gas. The annealing time depends on the cross-section; it increases as the square of the increase in cross-section.

H—O

$$\log K = \log p^2_{\text{H}_2\text{O}} / (p^2_{\text{H}_2} \cdot p_{\text{O}_2}) = 25,790/T - 5.85$$

Fe—H—O

Hydrogen in steel most probably results from the moisture in the furnace gases, slags and refractories and furnace additions. The extent of absorption depends upon the partial pressure of water-vapour in contact with (or diffusing through the slag layer to) steel and the state of oxidation of steel itself. The calculations are as follows :⁸⁸



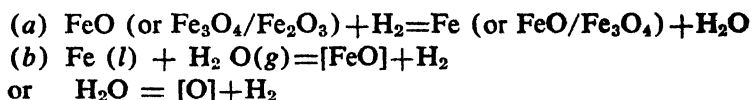
$$\log K = \log (\% [\text{H}])^2 \cdot (\% [\text{O}]) / p_{\text{H}_2\text{O}} = -10,380/T - 0.16$$

$$\text{At } 1,600^\circ \text{C or } 1,873^\circ \text{K, } K = 1.99 \cdot 10^{-6}$$

$$\text{Therefore, } \% [\text{H}] = 1.41 \cdot 10^{-3} \sqrt{p_{\text{H}_2\text{O}} / \% [\text{O}]}$$

Fig. 3.35 shows the extent of hydrogen absorption under different conditions of humidity and metal oxygen; higher the [O] the lower is the equilibrium [H].

The following reactions also belong to the Fe—H—O system :



The system (a) rather deals with the reduction of iron ores and, therefore, is of importance for Blast Furnace reactions. The

oxidation of iron by water or steam is governed by (b) and has importance, e.g. in Thomas converter using steam/oxygen or in

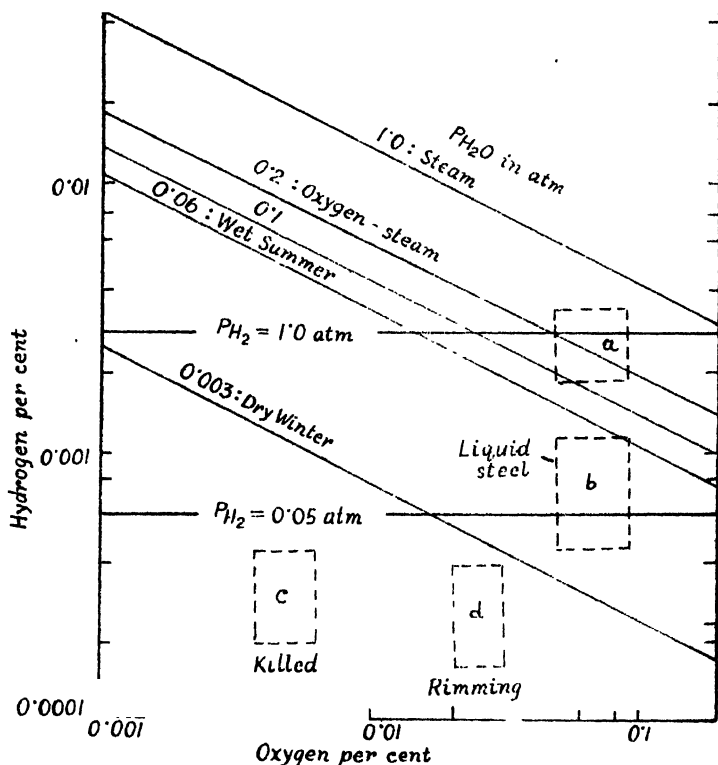


Fig. 3.35—Absorption of hydrogen in liquid steel from atmospheres containing moisture. The range of hydrogen contents of Thomas steels blown with oxygen/steam and in the finished products is also shown.

any steelmaking process where air containing moisture is used. The necessary data for (b) are :

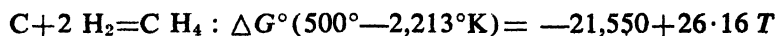
$$K_b = p_{H_2O} / (p_{H_2} \% [O] \cdot f_o)$$

$$\log K = 7,050/T - 3.17$$

$$\Delta G^\circ = -32,250 + 14.50 T$$

$$\text{where, } f_o^\circ = 1 - (2.51 - 1.19 \cdot 10^{-3} \cdot T) \cdot (p_{H_2O} / p_{H_2})^{2.89}$$

$$\text{or } \log f_o^\circ = -0.2 \% [O]^{.90}$$

C-H

$$\log K = \log p_{\text{CH}_4} / p^2_{\text{H}_2} = 4,710/T - 5 \cdot 71$$

Fe-N

Nitrogen in steel causes embrittling effects and impairs the impact strength after cold work and also the cold ductility values. The probable cause is strain-ageing caused by nitrogen in solution in ferrite. Steels blown by air in converters (containing 0.010—0.017% N) are, therefore, not suitable for cold drawing purposes like ship plates, car bodies, pipes, etc.

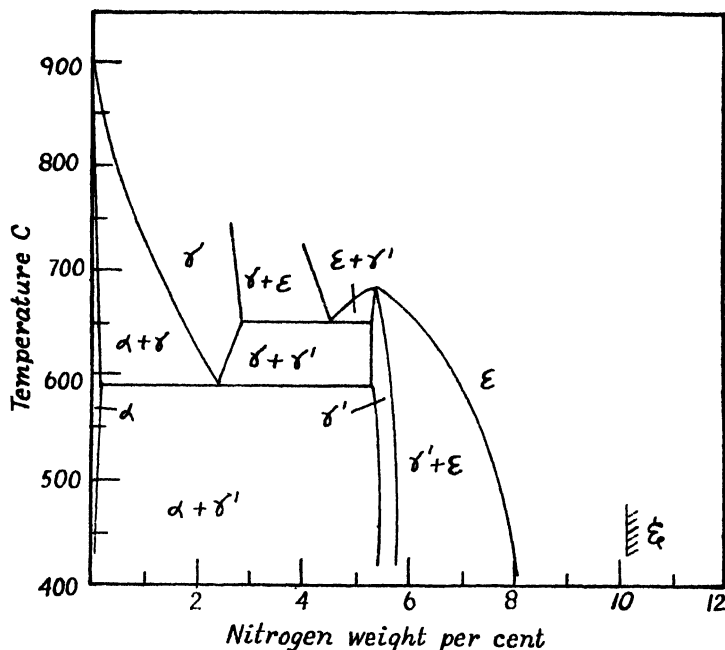


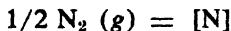
Fig. 3.36—Iron-nitrogen phase diagram. (V. G. Paranjape, M. Cohen, M. B. Bever & C. F. Floe, Trans. AIME, 188, 1950, 261).

The Fe-N phase diagram is shown in Fig. 3.36⁹¹

The solubility of nitrogen in steel, as in the case of hydrogen, is governed by Sievert's law :

$$p_{N_2} = (\% [N])^2 / K^2$$

The solubility is given in Fig. 3.33. The free energy of the reaction :



is $\Delta G^\circ = 2,200 + 5.26 T$ (for 1% hypothetical solution).

Dardell⁹² has given the following temperature-function of nitrogen solubility in liquid iron :

$$\log [N] = -1.161 / T - 0.722 + 1/2 \log p_{N_2}$$

where $[N]$ is in wt. per cent and p_{N_2} in atmospheres. At 1 atm, $\% [N] = 1.2 \cdot 10^{-5}$. $T + 0.0171$ in liquid iron.⁹³ On solidification to δ -iron the solubility decreases to about 0.0100%. According to Darken *et al.*⁹⁴ the solubility of nitrogen in γ -iron is more than that in δ -iron and it increases with decreasing temperature.

$$\% [N] (\gamma\text{-iron}) = 0.0404 - 1.2 \cdot 10^{-5} \cdot T$$

At the $\gamma \rightarrow \alpha$ transformation (910-925°C) the solubility falls abruptly to 0.0042%, while from the above equation it is 0.026% at 923°C.

Example :

At about 1,600°C, the solubility constant $K = 0.0396$.⁹⁵ Therefore, the evolution pressure for a steel with 0.010% $[N]$ is :

$$p_{N_2} = (0.010 / 0.0396)^2 = 0.064 \text{ atm.}$$

At 400°C, $K = 0.00018$. If the steel contains 0.010% $[N]$,

$$p_{N_2} = (0.010 / 0.00018)^2 = 3100 \text{ atm.}$$

At low temperatures the evolution pressure is enormous. It is obvious that a steel with high N-content is subject to a great stress at low temperature. The actual stress, however, depends upon the extent of decomposition of iron nitride (iron forms a compound Fe_4N) which is small especially at low temperatures.

The development of nitride needles (Fe_4N) is due to the falling temperature. Below 300°C only an iron sample containing

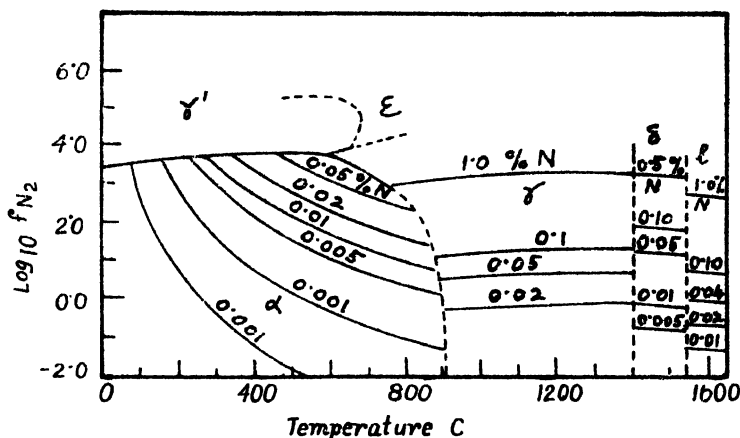
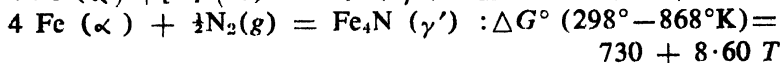
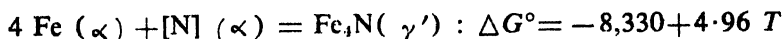


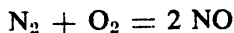
Fig. 3.37—Relationship between nitrogen content of iron and the various phases at different temperatures. (By courtesy of Steel & Coal).

0.01% nitrogen becomes saturated with the γ' -phase. Fig. 3.37⁹⁵ illustrates how iron nitrides are formed in steel containing even very low nitrogen. It further shows the metastability of γ' -phase (iron nitrides) and the impossibility of its formation at any nitrifying temperature ($p_{\text{N}_2} = 1 \text{ atm}$). The ease of formation of γ' iron nitride at ordinary temperatures even in the presence of traces of nitrogen is apparent from the iso-nitrogen concentration curves in the α -field. The ordinates in the figure are functions of nitrogen fugacity (f) which is approximately similar to nitrogen pressure at low pressure levels, but deviates markedly at high pressures due to non-ideality of nitrogen gas.

The free energies of the reactions are :⁹⁶



N—O



$$\Delta G^\circ = 43150 - 4.248 T - 0.282 T \ln T + 0.451 \cdot 10^{-3} T - 0.154 \cdot 10^{-6} T^3$$

Fe—N—O

It has been suggested that NO plays a part in the absorption of nitrogen in liquid iron,

$$\text{NO} = [\text{N}] + [\text{O}]$$

Therefore the nitrogen absorption at any temperature is dependent not only on the partial pressure of nitrogen but also on the oxygen content of steel. The more oxygen the bath contains, the less is the pick-up of nitrogen. Kosmider and Schenck⁹⁷ have shown that under reducing conditions the metal takes up nitrogen and under oxidising conditions it is removed. Naeser⁹⁸ explains the phenomenon on the assumption that iron forms an oxide film at the contact surface of iron and the oxidising medium ($\text{N}_2 + \text{O}_2$ or $\text{N}_2 + \text{CO}_2$) and this film prevents nitrogen pick-up.

However, Th. Kootz⁹⁹ and Naeser and Scholz¹⁰⁰ have now found that there is no chemical reaction between oxygen and nitrogen. Given sufficient time, even a highly oxidised metal will absorb a theoretical amount of nitrogen at $p_2 = 1$ atm. Naeser and Scholz suggest that since iron oxide reduces the surface tension of steel there is a preferential accumulation of the oxide of molecular thickness at the gas/metal interface which retards the velocity of nitrogen absorption.

Fe—N—X

Alloying elements have considerable effect on the solubility of nitrogen in steel (Fig. 3.38)¹. Carbon and phosphorus lower the solubility. While both chromium and vanadium increase the solubility, silicon at first increases and then decreases it¹⁰¹. The probable cause of the latter phenomenon may be the decreased solubility of nitrogen in presence of oxygen. At low concentrations of silicon the oxygen in steel is removed as silica, which increases the nitrogen solubility in the beginning; subsequently with more of silicon its effect in lowering the nitrogen takes its course.

The nitrogen affinity for some nitride-forming elements has already been given in Fig. 1.2. It enables one to form an idea of

the denitrifying power of the various elements. The behaviour of such elements in steel has been computed by Chipman⁷⁶. The calculated values of the equilibrium constant are given in Table 3.2.

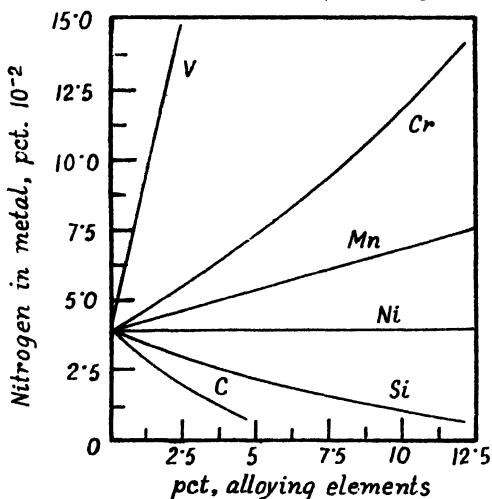


Fig. 3.38—Solubility of nitrogen in iron in the presence of various alloying elements at 1,600°C. (By permission from 'The Physical Chemistry of Metals' by L. S. Darken & R. W. Gurry. Copyright 1953. McGraw-Hill Book Co.).

Aluminium nitride AlN starts precipitating at a temperature where the observed product of $\%[\text{Al}]$ and $\%[\text{N}]$ equals or exceeds the equilibrium value. Si, B and V are not as good 'denitrifiers', but Ti and Zr form very stable nitrides which are cubic crystals without solubility in solid steel. Cr increases the solubility and decreases the ill-effects of nitrogen although unable to remove it to any extent.

TABLE—3.2^a

DENITRIFYING POWER OF ALLOYING ELEMENTS IN STEEL

Elements	Equilibrium Constant	Value at 1600°C
Aluminium	$\% [\text{Al}] \cdot \% [\text{N}]$	0.55
Boron	$\% [\text{B}] \cdot \% [\text{N}]$	Like Al
Silicon	$\% [\text{Si}] \cdot \% [\text{N}]$	14.00
Titanium	$\% [\text{Ti}] \cdot \% [\text{N}]$	0.00014
Vanadium	$\% [\text{V}] \cdot \% [\text{N}]$	1.5
Zirconium	$\% [\text{Zr}] \cdot \% [\text{N}]$	Like Ti

Fe-S

Sulphur possesses considerable affinity for iron. It forms FeS which is soluble in iron to a certain extent but exhibits a tendency towards immiscibility as indicated by the flattened solubility curve (Fig. 3.39)¹⁰². Sulphur activity also shows a positive deviation⁷⁶ from Raoult's law.

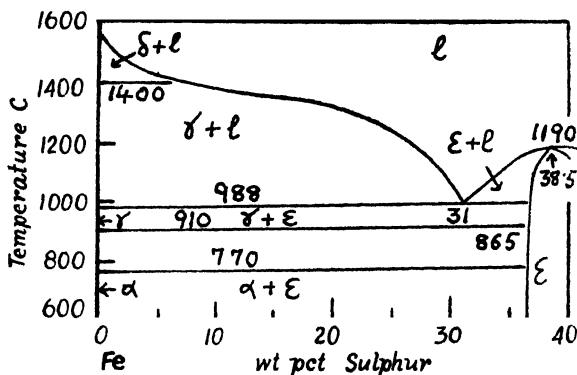
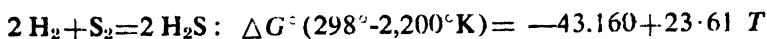


Fig. 3.39—Iron-sulphur phase diagram. (From 'Metals Handbook', ASM, Cleveland, 1948).

The Fe-S phase diagram shows a eutectic at 988°C (with ~ 31% S) between Fe and FeS. Sulphur solubilities in γ -iron are ~ 0.06% at 1,365°C and ~ 0.01 at 915°C^{103, 111}. Liquid iron with ~ 0.1% S starts freezing at 1,530°C and a sulphur bearing liquid phase starts separating when γ -iron is formed at 1,365°C. This separation continues until the eutectic temperature is reached when the whole system freezes. This low melting liquid during solidification probably precipitates around the metal grain boundaries and affects the hot rolling properties (red-shortness) leading to cracking or breaking of ingots.

H-S

Fe—H—S

The thermodynamical behaviour of sulphur in liquid iron has been mainly derived from equilibrium experiments with mixtures of H_2/H_2S in the temperature region of 1,550°-1,600°C. The reaction and the equilibrium constant are given by⁷⁶ :

$$H_2 + [S] = H_2S : \Delta G^\circ = 9,840 + 6.54 T$$

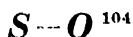
$$K = p_{H_2S} / (p_{H_2} \cdot \% [S]) : \log K = -2,150/T - 1.429$$

Here, in fact, $a_{[S]}$ should be used instead of % [S]. But Henry's law is obeyed below about 0.5% [S] and in this range the wt. per cent may replace the activity term.

Thus from the above equation, molten iron at 1,600°C would pick up as much as 0.4% S from an atmosphere containing only 0.1% H_2S .

Furnace gas in the open-hearth may contain sulphur in the form of H_2S , SO_2 , SO_3 , S_2 , COS and occasionally as HS and CS . The presence and relative proportions of any or all of these depend upon the temperature and oxidising/reducing condition of the gases, the latter condition being largely determined by the CO/CO_2 ratio and free oxygen present. At ratios between 1 to 0.01 the principal sulphur carrier is SO_2 . Under more oxidising conditions, SO_2 is oxidised to SO_3 .

Therefore, under the oxidising conditions prevailing in the open-hearth, a more realistic approach will be to consider the reaction of SO_2 with molten iron which is discussed in the next section.



$$O_2 + S_2 = 2 SO : \Delta G^\circ = -49,000 - 2.5 T$$

$$2 O_2 + S_2 = 2 SO_2 : \Delta G^\circ (298^\circ-2,200^\circ K) =$$

$$-173,240 + 34.62 T$$

Fe—S—O

The free energy of the reaction of SO_2 with liquid iron is :⁷⁶

$$SO_2 (g) \text{ 1 atm} = [S] + 2 [O]; K = [S].[O]^2 / p_{SO_2}$$

$$\Delta G^\circ = -1,340 - 12.81 T; \log K = 293/T + 2.8$$

Since the equilibrium constant of the equation is very high, about 10^{-3} at $1,600^{\circ}\text{C}$, almost the entire sulphur in furnace gases should go into iron. But this does not happen in open-hearth and it is presumed that the excess air forms an oxide layer which prevents or suppresses the sulphur absorption¹⁰⁵. Due to this, the above reaction does not reach equilibrium but a steady state is obtained obeying the following equation¹⁰⁶ :

$$\log (\% [\text{S}] / p_{\text{SO}_2}) = 2,642 / T + 0.350$$

The distribution of FeS between (FeO)-slag and metal is given by Bardenheuer and Geller¹⁰⁷ :

$$\log \% (\text{S}) / \% [\text{S}] = 2,390 / T - 0.714$$

Sulphur removal from metal to gas could occur only via the slag phase. In the open-hearth, this can take place during the melt-down period if the furnace gases are very oxidising and contain excess oxygen which enables the formation of a separate oxide phase. In fact the furnace atmosphere is not so oxidising and some fuel remains unburned due to incomplete combustion. As such the sulphur pick-up by steel mostly occurs during melt-down when the sulphurous gases directly impinge on the bare metal.

The Fe-O-S phase diagram¹⁰⁷⁻¹¹⁰ shows a miscibility gap with connodes sloping towards high sulphur. A liquid iron sample containing oxygen and sulphur on solidification leads to the separation of a sulphur-rich liquid oxide phase. On further cooling the oxide phase solidifies to form inclusive which, however, in contrast to FeS, do not tend so much to form on the grain boundaries. There is a low-melting (920°C) ternary eutectic in the system containing 7.9% oxygen and 24-25% sulphur^{109, 110}.

*Fe-Mn-S*¹¹¹

Manganese has always been considered as very beneficial for sulphur removal. Its role in desulphurisation has been discussed on pp. 300-306 and 318. It reacts with FeS according to :

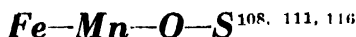


MnS melts at $\sim 1,600^{\circ}\text{C}$. It forms a eutectic with FeS at $1,170^{\circ}\text{C}$.

The solubility of sulphur in iron decreases in the presence of manganese. There is a wide miscibility gap in the Fe-Mn-S phase diagram.¹¹² MnS is not so harmful to 'red-shortness' as FeS because the former does not soften or liquefy at hot-working temperatures (because of higher melting point) and is not prone to form at the grain boundaries. There is a certain amount of manganese above which the presence of sulphur as FeS can be avoided. Although Whiteley¹¹³ indicates a ratio $\text{Mn}|\text{S} \sim 22$ for obtaining 100% MnS in the sulphide inclusions, normally a much lower ratio has been found to suffice in practice. The entire sulphur seems to be present as MnS, when

$$\% [\text{Mn}] = 0.3 + (1.7\% [\text{S}])^{114}.$$

Steel made for good machinability and free cutting properties contains sulphur as high as 0.3%. The presence of enough manganese in such steel is ensured so that the entire sulphur forms MnS inclusions. Machinability depends greatly upon the shape of the sulphide inclusions and increases as they approach spherical form. Small amounts of silicon help in the formation of fewer but larger lumpy inclusions which greatly improve the free-cutting properties¹¹⁵.



Steel always contains some oxygen and, therefore, the above system assumes importance in the formation of sulphide inclusions. If the $\text{Mn}|\text{S}$ ratio is such that it is possible for FeS to exist, there is a danger of formation of a low melting quaternary eutectic FeO-MnO-FeS-MnS (m.p. 910°C) which may cause troubles during hot working. Depending upon the $[\text{S}]$ and $[\text{O}]$ contents, either MnS or FeO-MnO solid solution can form, together with a high melting (above $1,290^{\circ}\text{C}$) eutectic of FeO-MnO-MnS.

The low melting inclusions can be avoided by an excess of Mn or by the removal of oxygen with strong deoxidisers like Al, Zr, Ti, etc. These elements also form sulphides like Al_2S_3 , $\text{FeS}.\text{Al}_2\text{S}_3$,

ZrS_2 , $2\text{FeS} \cdot \text{ZrS}_2$, TiS , CaS . They are all insoluble in steel and their amounts are also small.

FeO—MnO

The system is of importance in the deoxidation of steel with manganese. Depending upon the amounts of each, the deoxidation products may be solid or liquid as can be seen from Fig. 3.40(a)²⁷. The author has used this figure in computing the different zones of Fig. 3.9. There is no compound formation between the oxides and they form homogeneous liquid or solid solutions.

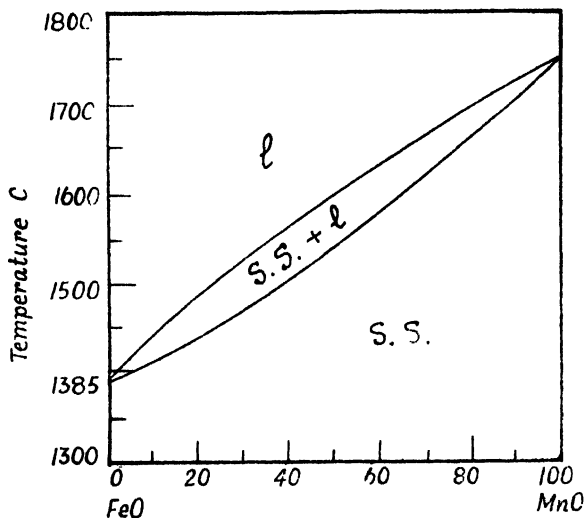


Fig. 3.40 (a)—FeO—MnO phase diagram.

FeO—MgO

The phase diagram of the above system (Fig. 3.40b)¹¹⁷ shows complete miscibility of the oxides in the solid as well as in the liquid state as in the case of FeO—MnO. It is clear that MgO is highly resistant to the corrosive action of FeO. Even at 1,700°C, about 94% FeO can completely liquefy MgO. Between 70-95%, a

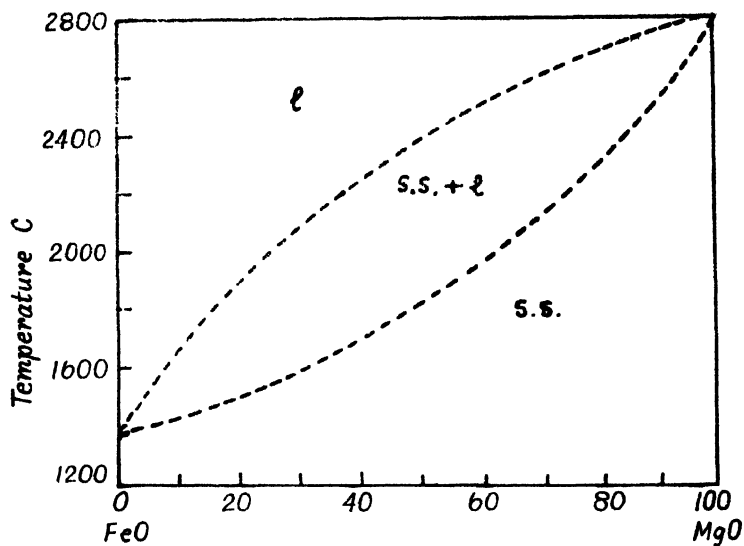
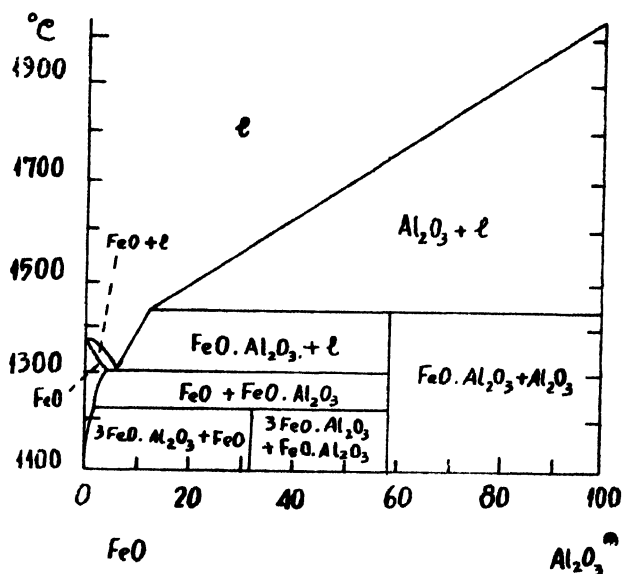


Fig. 3.40 (b)—FeO-MgO phase diagram.

Fig. 3.40 (c)—FeO-Al₂O₃ phase diagram.

two phase system exists, liquid FeO-MgO and solid MgO. Such a high (FeO) content never occurs in the basic slags.

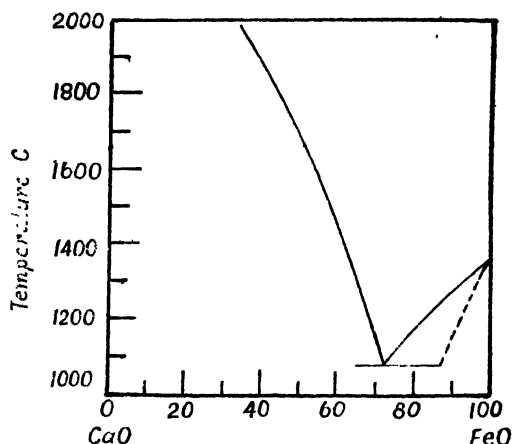


Fig. 3.40 (d) —CaO-FeO phase diagram.

$FeO-Al_2O_3$

The phase diagram of the above system (Fig. 3.40(c))⁷⁸ shows a low melting binary eutectic only at very high FeO contents. At 1,700°C, about 60% FeO will be necessary for the liquefaction of alumina. The system, however, changes on introduction of silica. A ternary eutectic of 40% SiO₂, 47% FeO and 13% Al₂O₃ has a melting point of only 1,073°C. Even with much smaller amounts of FeO, there are compositions of melting points less than 1,400°-1,500°C..¹¹⁶ Thus FeO can and does exhibit a powerful fluxing action on aluminosilicate refractories.

$FeO-CaO$

The above system (Fig. 3.40(d))¹¹⁸ shows a eutectic at $\sim 1,070^\circ\text{C}$ with $\sim 72\%$ FeO. The melting point increases sharply with increasing CaO and, at 1,700°C, as high as 50% FeO is necessary for the liquefaction of lime.

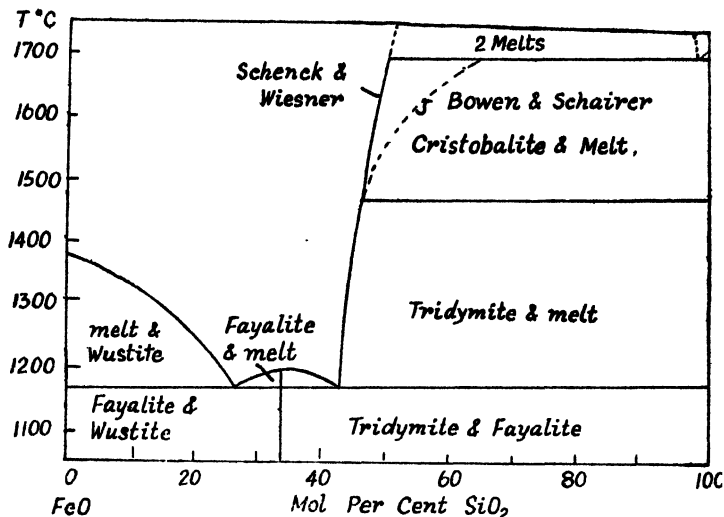


Fig. 3.41—The FeO-SiO₂ system. (H. Schenck & W. Wiesner. Archiv f.d. Eisenhuettenwesen, 26, 1956, 1-11).

$FeO-SiO_2$

From Fig. 3.41⁵, an iron silicate is saturated with solid silica with roughly 50 mol per cent of each in the range of steelmaking temperature. In wt. per cent the actual range is 50-55% FeO. The saturation concentration of Bowen and Schairer¹¹⁰ is shown by the dotted line. The steep saturation line shows that FeO can flux silica only to a limited extent.

$FeO-MnO-SiO_2$

This system (Fig. 3.42a)¹²⁰ is of importance in acid steelmaking as well as in the formation of inclusions when steel is deoxidised with silicon and manganese. As can be seen, the saturation value of SiO₂ does not vary much with the introduction of MnO in the FeO-SiO₂ system. Therefore, as MnO increases, FeO would decrease (the oxidising power would naturally decrease simultaneously), the silica content remaining more or less constant.

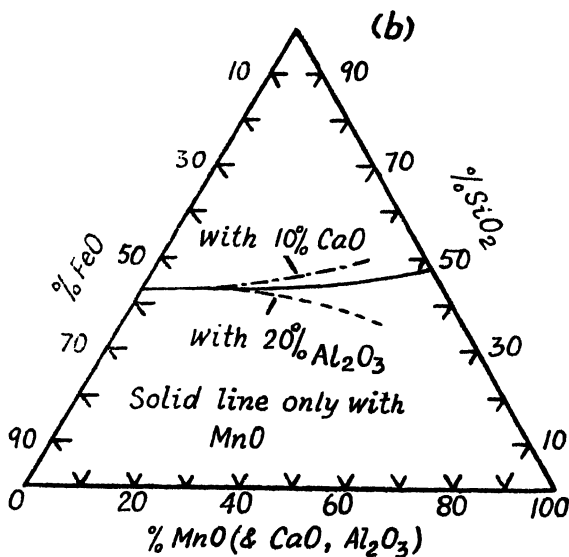
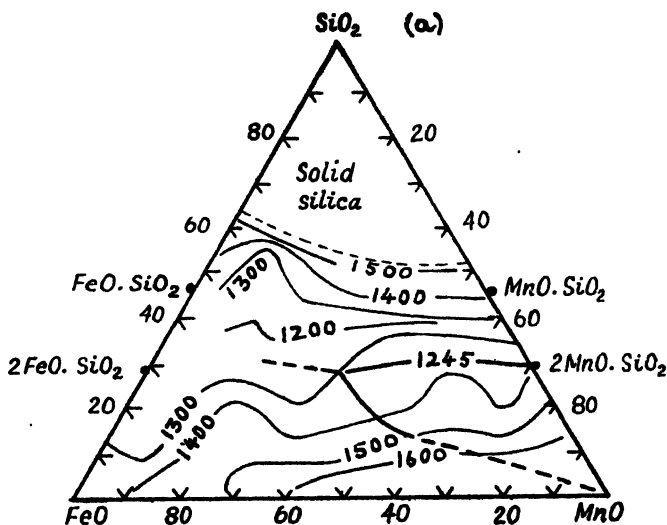


Fig. 3.42 (a)—FeO-MnO-SiO₂ phase diagram, (b) solubility of silica in FeO-MnO-SiO₂ slag in the pure system as well as in the presence of 10% CaO or 20% Al₂O₃.

The actual steelmaking slags are, however, always contaminated with lime and alumina. They respectively increase and decrease the solubility of silica in FeO-MnO-SiO_2 slags (*cf.* Fig. 3.42 (b)).⁵

The temperatures of liquidus surfaces are also drawn in Fig. 3.42(a). There is a ternary eutectic in the system melting at $1,170^\circ\text{C}$ having a composition of 47% FeO , 20% MnO and 33% SiO_2 . Low melting deoxidation products below $1,200^\circ\text{--}1,300^\circ\text{C}$ are possible. There is a possibility of the existence of a compound $2\text{MnO}\cdot\text{FeO}\cdot\text{SiO}_2$ melting at approximately $1,400^\circ\text{C}$ having a rough composition of 25% FeO , 53% MnO and 22% SiO_2 .

CaO-FeO-SiO_2 ⁶⁴

This system (Fig. 3.43) is of importance in basic open-hearth steelmaking. The actual slag, however, consists of eight or nine components and it is impossible to put them in a ternary diagram. About 80% is made of CaO , SiO_2 , FeO and the rest 20% are MnO , MgO , Al_2O_3 , P_2O_5 etc. The pure system as given in the figure may serve as a guidance if MnO is taken with FeO , MgO with CaO and Al_2O_3 with SiO_2 because of their similarity in physical properties.⁶⁴

Fig. 3.43 shows the liquidus temperatures as well as lime saturation line A of Körber and Oelsen¹¹⁸ at $1,600^\circ\text{C}$ for the pure system and that of Speith *et al.*¹²¹ (B) at $1,700^\circ\text{C}$ for the actual slag, the constituents having been converted to 100%, i.e. ($\text{CaO}' + \text{FeO}' + \text{SiO}_2' = 100$). Line B approximately corresponds to $\text{CaO}|\text{SiO}_2 = 4$ up to about 30% FeO or 37% FeO' . The liquidus temperatures shown will also be less in actual slags because of the presence of fluxing components like ferric oxide, fluorspar, alumina.

The broken lines C and D show the compositional changes undergone by slags in with-ore and no-ore heats.⁶⁴ Both these lines pass through low melting zones where the slag must be very fluid. As the heats proceed and increasing amount of lime dissolves, the melting zone rendered viscous with refractory tricalcium silicate is reached. The curves move towards the FeO -corner in the end not only because the progressive removal of

carbon to low values requires increasing iron content in slag (*cf.* Fig. 3.7) but also higher slag iron is necessary for dissolving more lime to meet the demand of the finishing slags.

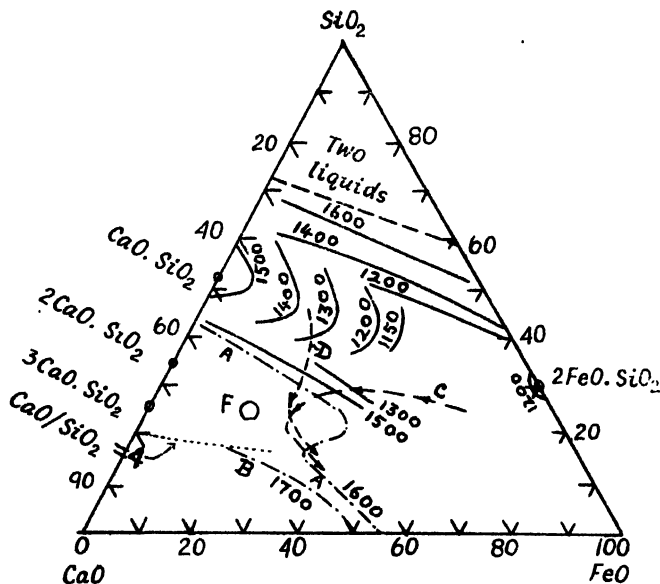


Fig. 3.43—FeO-CaO-SiO₂ system. For details see text.

A qualitative comparison of Fig. 3.43 with the (FeO)-activity diagram (Fig. 4.4(a)) shows that the initial high iron acid slag in ore-practice, line C, is highly oxidising. Such a slag is capable of phosphorus removal though it is acidic. The activity of (FeO) decreases as metalloids continue to react and small amounts of lime dissolve, with the danger of phosphorus reversion. Such a slag is, therefore, usually flushed off.

It must be noted that an increasing iron in the slag at the finishing-stage would deliver an increasing amount of oxygen to the metal which has to be removed by deoxidisers. For lowering the *final* or *residual* oxygen, the author suggests refining towards *F* after the flush off. From Fig. 4.5 the activity of (FeO) is maximum at $\text{CaO/SiO}_2 \sim 2.7$ for any given iron content and a profuse carbon boil could be attained which would lower the iron content of slag and, therefore, the oxygen content of steel. Figs. 3.43 and

4.4a show that the direction of F is towards a lower (FeO)-activity.

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THE STEELMAKING SLAGS

THE production of steel is mainly a process of refining pig iron by a selective oxidation of the various impurities. We have already discussed in Chapter II that the oxidation of the dissolved elements produces insoluble oxides, both acidic and basic, which combine with added lime, fluorspar or other fluxes to form slag. The slag always contains FeO also formed from the oxidation of iron. This oxide has a minor solubility in steel which is of extreme importance since it is the principal oxidising agent.

In converter process, the amount of air blown-in is more or less constant and the oxygen potential of the oxidising agent, therefore, remains a constant quantity from the beginning to the end. As such the rate and the extent of oxidation cannot be altered at will. The slag in such a process serves only as a reservoir for the unwanted impurities and its composition is so adjusted that no reversion of these impurities to the metal may occur at the end.

The extent of removal of the elements depends upon the equilibrium relations between the slag and metal constituents. Therefore, the activities of the slag constituents and the influence of slag composition on them are of primary importance in any steel-making process. Since the refining is performed primarily by oxidation, the oxidising power of slag has attracted the attention of all steelmakers.

In open-hearth refining process the slag plays the most important role. Since the oxygen carrier is FeO , it is the so-called 'free ferrous oxide' or the activity of (FeO) in the slag which determines the amount of $[\text{FeO}]$ or $[\text{O}]$ in iron and consequently controls the oxidation processes. Thus, in the open-hearth the rate and extent of oxidation can be controlled at will by suitably adjusting the activity of (FeO) which may be effected through changing the composition of the slag, e.g. by the addition of oxidising agents (like ore) or by additions such as lime which lowers the oxide activity of basic slags. In extreme cases, the oxidation potential is nullified by additions of strong reducing agents

like CaC_2 , Fe-Al, Fe-Si to the slag (as in electric furnaces). The oxidising power of slag, however, does not always determine the oxygen potential of the bath. The carbon and to a small extent phosphorus contents (at low carbon level) determine the oxygen-content of steel.

Apart from the effect of chemical conditions and temperature, the viscosity of the slag is also of importance. A viscous slag hinders rapid oxygen transfer to the bath in the hearth furnaces and causes considerable build-up of oxygen in the slag as higher iron oxides. Such a slag may be troublesome, as it starts delivering oxygen to the metal during the later part of the refining period when the slag becomes fluid due to increased temperature and iron-content. Further, the reactions between the metal and the slag take place at the slag metal interface; and such reactions are facilitated by the diffusion of the elements and/or compounds to the interface which becomes easier, the higher the fluidity of the metal and the slag. The area of the contact surface has also a profound effect on the rate of the reaction. If iron is poured into slag as in the Perrins process¹ for dephosphorisation, the reaction is almost immediate. It is, therefore, not only the amount of oxygen-carrier in the slag but also the relative ease with which it can diffuse and reach the metal surface as well as the extent of the slag-metal contact surface that determine the ultimate rate of oxidation. It has been suggested that the better desulphurisation in basic processes at high temperatures is not so much due to the chemical reactivity as the increased fluidity of the slag. The high fluidity enables the slag sulphide produced at the slag-metal interface to distribute itself readily throughout the slag medium by diffusion. Increasing the fluidity by raising the temperature and by addition of suitable flux or ore must, however, be performed taking into consideration the steel quality, slag bulk and economy of the process.

The important oxides which make up the slags in the steelmaking processes are divided into three categories : acidic, basic and neutral or amphoteric. A table is given below of the compounds believed to be belonging to these categories :

Acidic	— SiO_2 ; P_2O_5 ; Cr_2O_3 ; V_2O_5
Basic	— CaO ; MgO ; FeO ; MnO
Amphoteric	— Al_2O_3 ; (Cr_2O_3) ; V_2O_4 ; Fe_2O_3 .

It is difficult to place some of the oxides in a definite group. The oxides Cr_2O_3 and Fe_2O_3 behave sometimes as acidic and are taken as such under certain circumstances. According to Schenck,² MgO behaves as acidic at high temperatures and, therefore, it may belong to the amphoteric group. The place of V_2O_3 has not yet been definitely allotted.

If the slag contains oxides predominantly of the first category it is called acidic and if predominantly of the second it is basic. In general, the acidity or basicity of a slag is determined by the ratio (basic oxides in wt. %)/(acid oxides in wt. %). If the ratio is more than about 1.1-1.3 it is termed basic and if less than 1 it is acidic (without taking Al_2O_3 into account). Acidity or basicity in metallurgy has, however, no absolute value: while a certain ratio is deemed acidic in a certain process, the same ratio may be taken as basic in some other. In fact, the modern ideas about slag tend to make it rather unacceptable that either the acidity or basicity is a criterion for its behaviour. It is most probable that the activities of the slag constituents such as CaO , SiO_2 , MnO , FeO and others play the dominant role.

Since the impurities of iron are oxidised away to the slag it is natural that iron in its turn would endeavour to reduce them to the metal until a state of dynamic equilibrium between the slag and the metal is reached. Chemical changes occurring in the steelmaking processes are reversible and, therefore, cannot proceed beyond equilibrium. A knowledge of slag-metal equilibria can predict the ultimate composition of the metal under definite sets of conditions and the composition will not vary until the prevailing temperature and slag compositions are changed. It is possible by suitable adjustments of slag and temperature to obtain a desired steel composition and, therefore, a desired steel quality. Sometimes, however, a suitable compromise has to be made since one set of conditions may be favourable for one reaction and unfavourable for another. Although a knowledge of the equilibrium constant does not predict the velocity of a reaction, it may still be useful for investigating the conditions under which the reaction may approach the equilibrium as far as possible, if in practice it has not proceeded as far as desirable. The study of slag-metal equilibria has gone a long way to roughly predict the distribution of Mn, P, Cr, etc. and the influence of temperature

and slag-metal compositions on them. A quantitative relationship of the distribution of any element between the slag and the metal enables us not only to control the progress of a heat in order to obtain steel conforming to the specifications but also to reduce the slag bulk and the loss of valuable alloying elements in the slag.

The equilibrium constant is found by using mol fractions in place of concentrations in the *L.M.A* (Law of Mass Action) equation in the case of ideal solutions. If the components mutually influence each other, the concentration terms are substituted by the respective activities. The concentrations of elements in the metal are usually small and are, therefore, expected to obey the Henry's law and their weight percentages are used in the equation. The mol fractions are calculated as follows :¹³

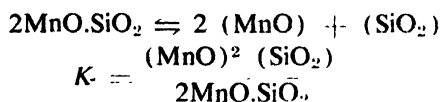
Suppose a slag contains $\text{CaO} = 38.2\%$, $\text{MgO} = 9.5\%$, $\text{MnO} = 6.8\%$, $\text{FeO} = 8.0\%$, $\text{SiO}_2 = 21.9\%$, $\text{P}_2\text{O}_5 = 13.5\%$ and $\text{Al}_2\text{O}_3 = 2.0\%$. The alumina-content is neglected in the calculations of mol fractions. Therefore, the rest of the components are converted to values on 100% basis and further calculations follow as shown in Table 4.1.

TABLE—4.1

Slag Component	Gram moles	Total for 100 gm slag	Mol fraction
CaO	$38.96/56 = 0.696$	1.618 moles	$0.696/1.618 = 0.43$
MgO	$9.69/40 = 0.242$		$0.242/1.618 = 0.15$
MnO	$6.93/71 = 0.098$		$0.098/1.618 = 0.06$
FeO	$8.16/72 = 0.113$		$0.113/1.618 = 0.07$
SiO_2	$22.31/60 = 0.372$		$0.372/1.618 = 0.23$
P_2O_5	$13.77/142 = 0.097$		$0.097/1.618 = 0.06$

The use of concentration terms in the *LMA* equation very rarely gives 'nonvariable' constants. This is also not expected since the slags are composed of various oxides some of which

are acidic and some basic in behaviour and it is but natural that they will combine and form compounds. Schenck² assumes that the most important compounds formed are $2\text{FeO}.\text{SiO}_2$, $2\text{MnO}.\text{SiO}_2$, $\text{CaO}.\text{SiO}_2$, $3\text{CaO}.\text{P}_2\text{O}_5$ or $4\text{CaO}.\text{P}_2\text{O}_5$ and $(\text{CaO})_m . (\text{Fe}_3\text{O}_4)_n$. He takes these compounds into account in his investigations on the derivation of his theory of slag|metal equilibrium. The compounds formed from the combination of the oxides do not use up all the simple reactants but certain amounts or proportions remain behind in an uncombined state, or as better known, *free* state. Such an assumption is not contrary to the physico-chemical laws since, according to the equilibrium concept, there must be a certain ratio between the concentration of the compound formed and that of the 'free' or uncombined original reactants. Thus, two oxides, the acid SiO_2 and basic MnO , when melted together give a compound $2\text{MnO}.\text{SiO}_2$ or conversely, when the compound is melted, it dissociates to a certain extent into the respective oxides, the equilibrium equation being :



It is clear that some MnO and SiO_2 are always in the *free* state, however small the quantity may be. But it is almost impossible to determine the free quantities by chemical analysis. Chemical analysis is performed on solidified slags in which the nature and proportion of the constituent compounds may widely vary from those of the high temperature liquid slags.

The chemical analysis gives only the total concentrations such as 'total lime', 'total phosphorus' 'total silica' etc., which are written as ΣCaO , $\Sigma \text{P}_2\text{O}_5$, ΣSiO_2 etc. The 'free' quantities are written as (CaO) , (P_2O_5) , (SiO_2) , (FeO) , etc. The total concentrations have to be separated into free quantities and residual compounds so that the *LMA* can be applied. This theory of 'free' quantities as applied to steelmaking slags is known universally as the Schenck's theory of *free oxides*. The compounds assumed to be present in slags are supposed to be in equilibrium with the 'free' component oxides.

The dissociation constants of these compounds were found by

Schenck, assuming that the *LMA* was applicable to liquid slags, mostly from a mass of steelmaking data by empirical methods of trial and error and finding the best fits. With the help of these results he constructed charts² at various temperatures relating the 'free' constituents of slags to the total concentrations found from analysis. The free components when used in the *LMA* equations for various steelmaking reactions furnish reasonably non-variable constants. The use of Schenck's figures will be found in the text at appropriate places.

Free FeO

The concentration of ferrous oxide FeO in the slag is of fundamental importance for determining the oxidising or the reducing capability of the slag and also for the transfer of oxygen from slag to metal. The relation between free (FeO) and [O] or [FeO] is given by Körber and Oelsen's³ constant *L* at various temperatures. For 1,600°C, $L = \% (\text{FeO}) / \% [\text{O}] = 450$ or $\% (\text{FeO}) / \% [\text{FeO}] \sim 100$.

Free (FeO) in acid slags : The acid steelmaking slags consist mainly of FeO and MnO saturated with SiO₂ (over 50%) together with about 10-12% CaO and Al₂O₃ of which the major portion is CaO. In the acid open-hearth, the rate of decarburisation is slower than in the corresponding basic process, although the total iron content of the slag is much higher in the former. This suggests that the [FeO] in the metal, which determines the rate of carbon drop, is less in the acid process; and as [FeO] is related to (FeO) by the partition constant, the *free ferrous oxide* (FeO) of the slag on its part must also be less. It can naturally be concluded that only a certain portion of the total FeO-content of the slag exists in the free state and the rest is combined with SiO₂ (since FeO does not form compounds with MnO). Figs.² 4.1(a) & (b) show the lines of constant free-(FeO) in acid slags at 1,577° and 1,627°C. The figures for slags with 10% neutral constituents are not included here but they show slightly higher (FeO).

Free (FeO) in basic slags : The basic open-hearth slags consist of FeO, Fe₂O₃, MnO, CaO, P₂O₅, SiO₂, MgO, Al₂O₃ together

with CaS and CaF_2 . The presence of so many substances in the slag makes it difficult to ascertain the free- (FeO) content of the slag. Further difficulties can be attributed to the presence of Fe_2O_3 which is generally supposed to be formed from the FeO on oxidation by the heating gases.

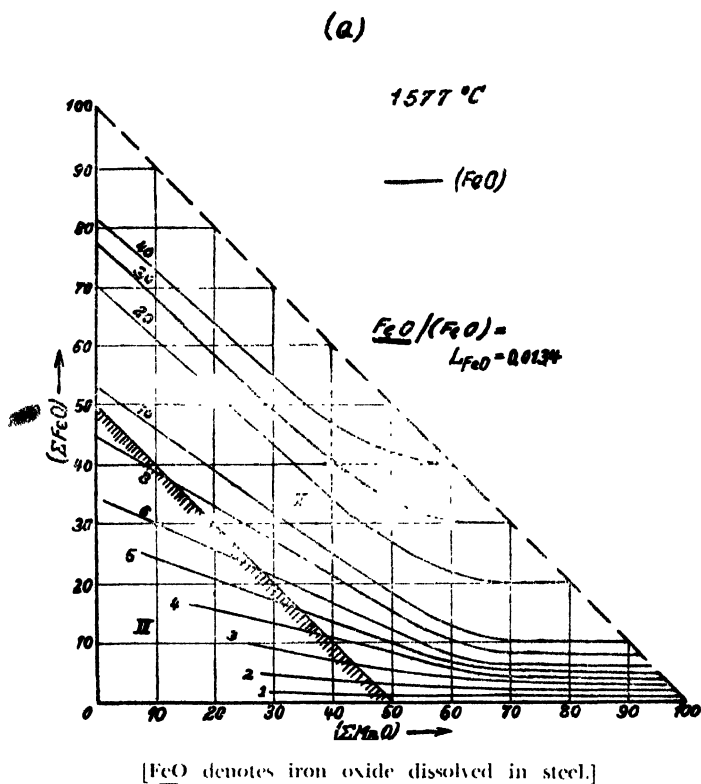


Fig. 4.1(a)—Concentrations of free (FeO) in FeO-MnO-SiO_2 slags at 1577°C. The silica saturation line is according to Korber & Oelsen. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

Schenck derived relationships between (FeO) , the total iron content (ΣFe) which is an analytically determined quantity, the other remaining slag constituents and the temperature. He did not take into account the presence of compounds like Fe_2O_3 or Fe_3O_4 at steelmaking temperatures in contact with liquid iron, or

of compounds of iron oxides with MgO , Al_2O_3 , P_2O_5 etc. Fig. 4.2² shows the relevant data.

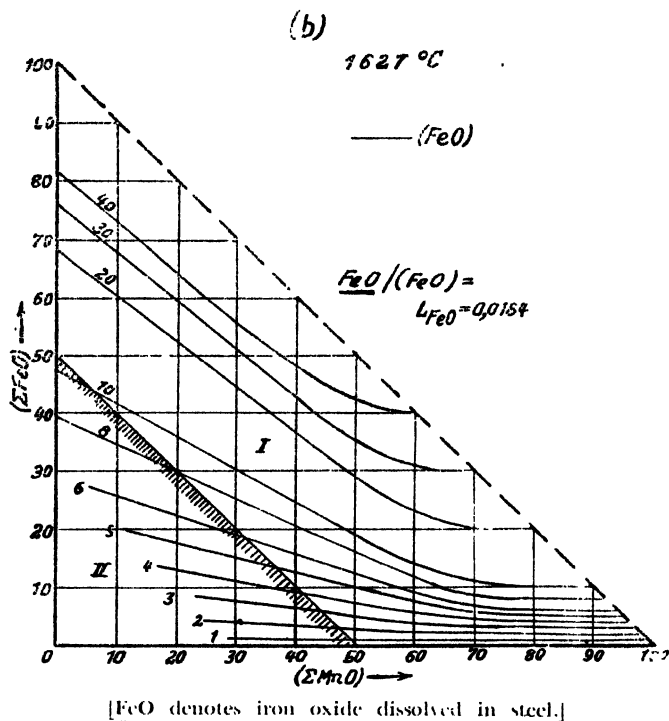


Fig. 4.1(b)—Same as Fig. 4.1 (a), at 1,627°C.

Schenck and Riess⁴ suggest that some lime combines with iron as a ferrite in the form of $(\text{CaO})_m \cdot \text{Fe}_3\text{O}_4$ where m can have values from 1 to 4. They have taken an average value of $m = 3$ which agrees well with their calculations.

Free and Combined Silica

Although it is possible for silica to combine with MgO , Al_2O_3 and other minor basic and amphoteric oxides, their compounds have been neglected by Schenck and Riess⁴ for deriving the free silica values. Instead of giving the free silica values, they have indicated directly the Mn- and Si-contents of the metal in contact with slags of different compositions, as shown in Figs. 4.2 and 6.7.

Fig. 4.2 shows the free lime in basic slags.

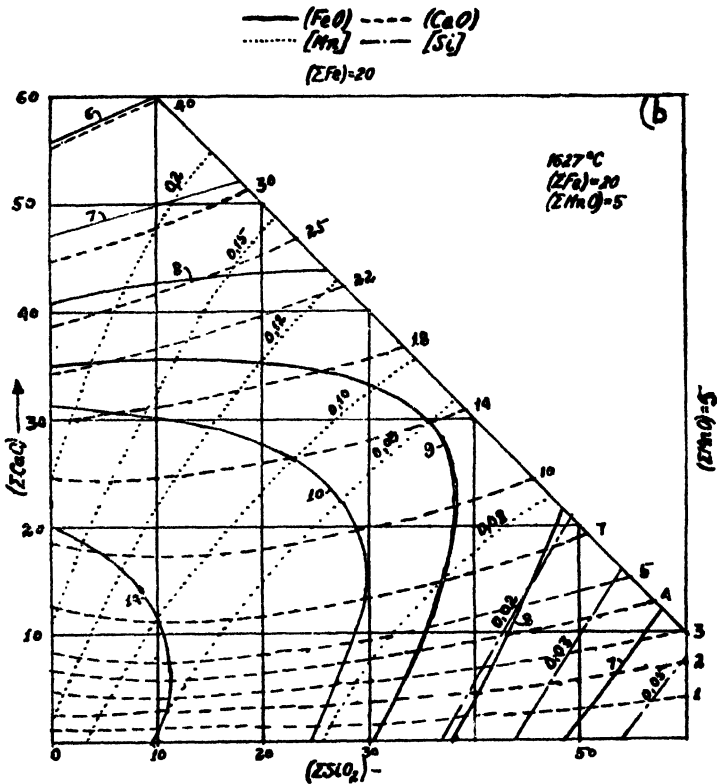


Fig. 4.2(b)—Same as Fig. 4.2(a), for 20% (ΣFe) and 5% (ΣMnO) in the slag.

Combined Phosphoric acid or phosphates

Phosphates in slag on analysis are represented as P_2O_5 . For all practical purposes the P_2O_5 is combined with CaO as tri- or tetra-phosphate or both. There is none or a negligible quantity of P_2O_5 in the free state, if not for any other reason, at least due to the high vapour pressure of P_2O_5 .

Schenck assumes the presence of $4\text{CaO} \cdot \text{P}_2\text{O}_5$ for mathematical simplicity and as such the phosphorus equation should be as given in the preceding section.

Free and Combined MnO

MnO forms with silica only an orthosilicate— $2\text{MnO} \cdot \text{SiO}_2$. The manganese in the metal, instead of free MnO in the slag, is shown in Figs. 4.2 and 6.7.

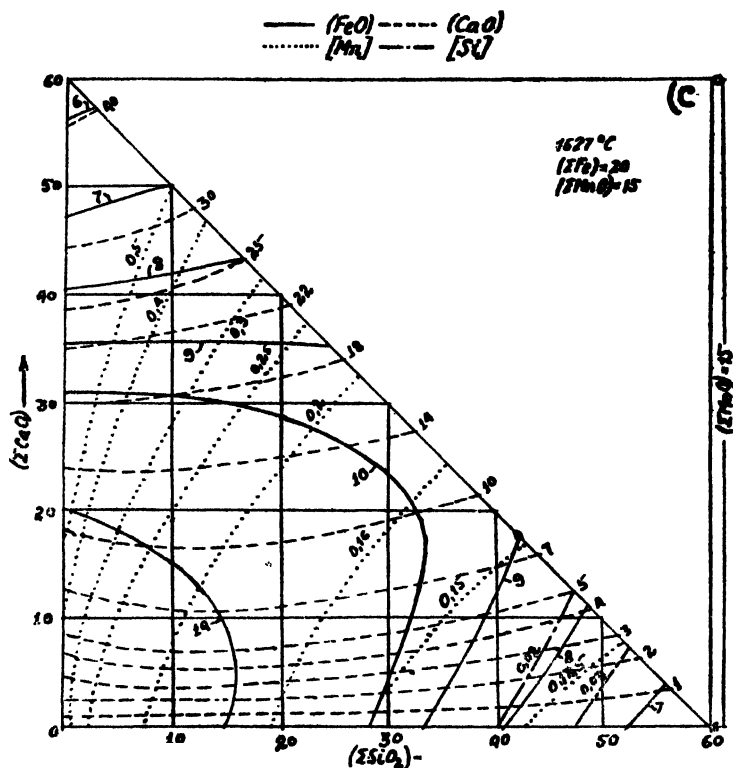


Fig. 4.2 (c) --Same as Fig. 4.2 (a), for 20% (ΣFe) and 15% (ΣMnO) in the slag.

The use of free quantities in the *LMA* equations presupposes the ideal behaviour of slag. It is true that the values calculated by Schenck and others with this assumption are of great practical applicability because the equilibrium constants themselves have been found out from a mass of steelmaking data by trial and error methods. But, in fact, all the slag constituents do not behave ideally, especially at high concentrations. Schenck's concept of slags as combinations of various oxides, with ultimate electro-

neutral compounds, contradicts also the findings which show conclusively the electrical character of the slags. Slags have been found to conduct electricity and dissociate into ions.

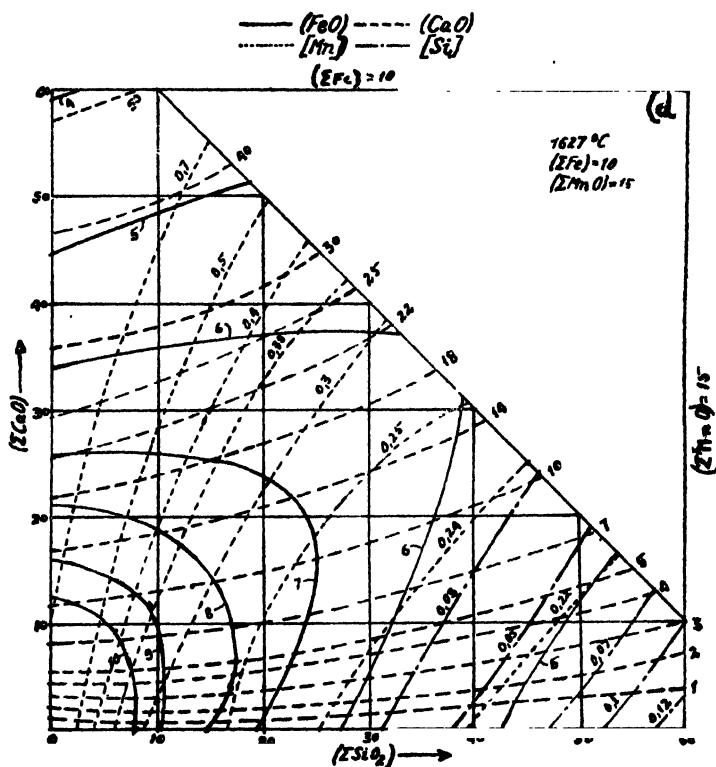


Fig. 4.2(d)—Same as Fig. 4.2(a), for 10% (ΣFe) and 15% (ΣMnO) in the slag.

The proper non-variable constant can only be obtained if, in place of the concentrations, the activities of the reacting substances are used. The principal difficulty in the application of physico-chemical laws, for ascertaining the equilibria in the metal/slag and slag/gas reactions, has been the lack of knowledge of proper activity values of the various substances involved in the metal/slag/gas phases at steelmaking temperatures.

It is, however, true that certain specific slags, formed from oxides, behave ideally and the activities of the constituent oxides approach their mol fractions. This may happen in slags where

the oxides show solid and liquid solubilities in wide ranges of compositions, as for example, in the FeO-MnO system (Fig. 3.40a). The equilibrium constant K of the system $(\text{FeO}) + [\text{Mn}] = (\text{MnO}) + [\text{Fe}]$ has been found to be nonvariable by taking the mol fractions of FeO and MnO in the pure FeO-MnO slag.

In the FeO-MnO-SiO₂ acid slags, the (FeO) behaves ideally, i.e. the mol fraction of (FeO) is approximately equal to its activity, although FeO and SiO₂ form silicates. The reason for the applicability of Raoult's law in this case may be that, at high temperature and in the liquid state, the silicate is completely dissociated. That $L = \%(\text{FeO}) / \% [\text{O}]$ is a constant (*cf.* p. 9) even with an acid slag,^{3a} can only mean that (FeO) must be present in a 'free' or uncombined state in such a slag.

Various workers⁵⁻⁷ have shown that the activity of FeO does not follow Raoult's law in acid slags—FeO-SiO₂, FeO-Al₂O₃-SiO₂, etc. Attempts have been made to elucidate the constitution of basic slags on the assumption that the (FeO) behaves ideally^{8,9}; and any deviation from the Raoult's line does not necessarily mean that such slags are not ideal with regard to (FeO) but, rather, the methods of calculations for finding the mol fractions are at fault. Efforts have been made to find out the constitutions of various slag compounds which give the values of the mol fractions of (FeO) that tend to follow the Raoult's law when plotted against the FeO-activity.

Taylor and Chipman¹⁰ have studied the FeO-activity in the basic slag CaO-FeO-SiO₂ that contained MgO and Fe₂O₃ as impurities. Their activity diagram in the ternary system is similar to that of Turkdogan and Pearson¹⁰ (see Fig. 4.4a) and shows a symmetry of the iso-activity lines about the composition of 2CaO.SiO₂. For a basic slag containing CaO more than that necessary for the formation of the compound 2CaO.SiO₂, an assumption of the presence of the following compounds has been made, viz: CaO, CaFe₂O₄ and 2CaO.SiO₂. A plot of the activity of FeO against the mol fraction on such an assumption shows a deviation from the Raoult's line. If, however, it is imagined that 2CaO.SiO₂ exists as doubly associated, i.e. (2CaO.SiO₂)₂ or Ca₄Si₂O₈ and the activity and the mol fraction of FeO replotted, the Raoult's line is very closely approached as shown in Fig. 4.3^{9a}.

It is a matter of doubt whether FeO actually behaves ideally in

slags. It is true, in some cases satisfactory equilibrium relations have been obtained in the slag-metal systems, but it must be admitted that in calculating the concentrations such as 'free FeO',

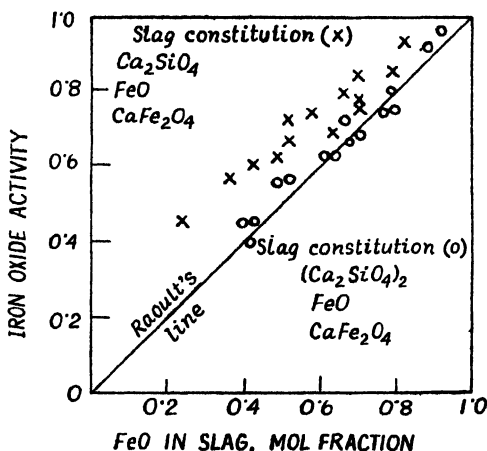


Fig. 4.3—Activity of FeO in liquid basic slags assuming two different combinations of lime & silica. (G. Derge & M. Tenenbaum, Basic Openhearth Steelmaking, AIME, Copyright 1951).

'free CaO' and the like, arbitrary assumptions have been made regarding the slag constitutions. Because of such assumptions, these equilibrium relations hold good only for certain slag and metal compositions and fail in other cases where the real concentrations do not correspond with the activities.

If, in the place of molal concentrations, the activities are used, there is no need of making any arbitrary assumptions about the constitution of the slag *vis a vis* the slag composition. It is enough to know the change of the activities of the various constituents taking part in slag-metal reactions with varying slag compositions. The use of the activity method in equilibrium calculations has been discussed for manganese, phosphorus and other reactions. The activities of some slag components in different slags are given in the following sections.

Activity of FeO

The activity of FeO in steelmaking slags is measured by the ratio of the actual oxygen content of iron under the particular

slag to the maximum solubility of oxygen under pure-FeO-slag at that temperature (cf. p. 64). Calculations made on this basis, with slags of different compositions, give iso-activity curves which are useful for practical purposes. The activities and activity co-efficients of FeO for basic and acid slags are given below.

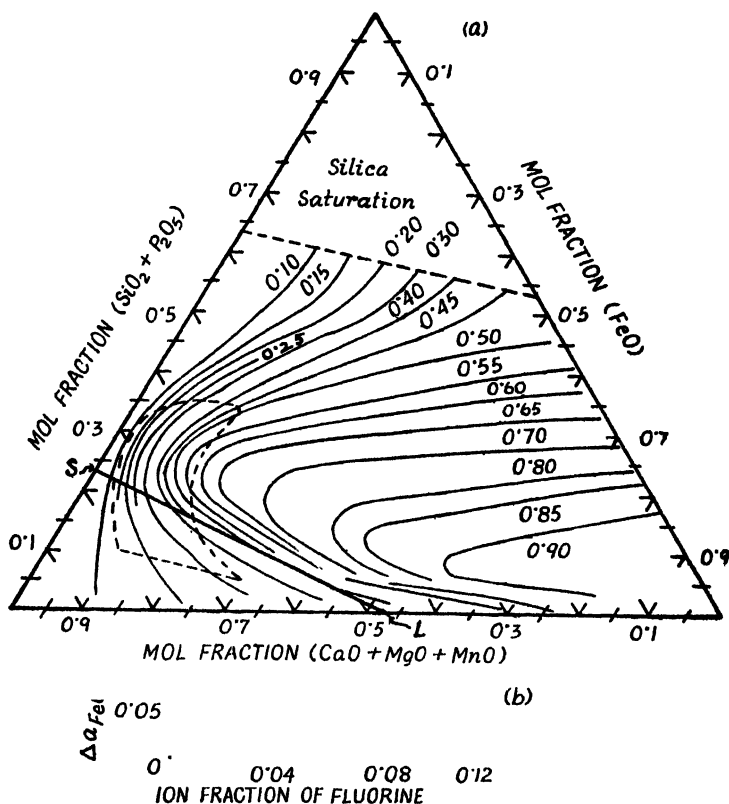


Fig. 4.4—(a) Activity of iron oxide in basic slags (Turkdogan & Pearson). Area inside dotted line represents common basic openhearth slags. Line LS represents approximate lime saturation in such slags.
(b) Effect of fluorine on FeO activity (Pearson).

Basic open-hearth slag^{9,10} : It has been found that the bases CaO, MnO, MgO are equivalent as regards their effects on the activity of FeO, i.e. it is not their individual concentrations but rather the total concentrations in terms of mol fractions that

matter. Similarly SiO_2 and P_2O_5 , provided the latter is less than 0.1 mol fraction, are equivalent. Al_2O_3 has apparently no effect and the mol fractions are calculated without taking it into consideration. Any Fe_2O_3 present, is converted into FeO and added to the analytical FeO -content ($\text{FeO}_{\text{total}} = \% \text{FeO} + 1.35 \% \text{Fe}_2\text{O}_3$). The bases and the acids and the FeO thus calculated, form the three corners of a pseudo-ternary diagram. The (FeO) -activity, found from the oxygen analysis of pure iron equilibrated under each slag composition, is drawn in the figure. The iso-activity lines of (FeO) thus found are shown in Fig. 4.4¹⁰. It may be mentioned here that the a_{FeO} is independent of temperature. The area inside the dotted line represents common basic open-hearth slags. The line LS shows the approximate lime-saturation at steelmaking temperatures.¹¹ It is, however, not readily apparent how a_{FeO} changes with the basicity and the iron oxide content of the slag. In order that the figure may be useful for practical purposes, Fig. 4.5¹² has been drawn. It is clear from the figure that the a_{FeO} increases with the (FeO) -content of the slag and that, for any given (FeO) -content, the activity increases with increasing basicity in the acid-range but decreases in the basic-range slags.

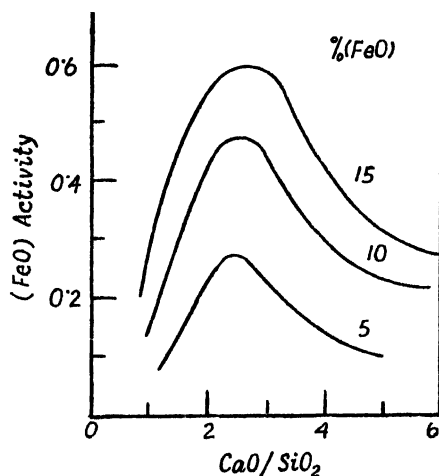


Fig. 4.5—Dependence of FeO activity on basicity.

It has been found that fluoride ions, from the additions of fluorspar to basic slags, increase the a_{FeO} in comparison with

fluorine-less slags by an amount Δa_{FeO} (can be estimated from Fig. 4.4b). The term ion fraction in Fig. 4.4b¹³ is found by dividing the weight of F in 100 gm of slag by its atomic weight (19) and further calculations follow as with other mol fraction values. The lime part of CaF_2 is included in the mol fraction of CaO . The preliminary value of a_{FeO} is found with the help of Fig. 4.4a from the mol fractions of (CaO , MnO , MgO), (SiO_2 , P_2O_5) and (FeO) to which is added Δa_{FeO} for calculating the actual a_{FeO} .

Thomas slags : The activity of FeO in Thomas slags is determined in the same manner as in basic open-hearth or other slags. The subject has been discussed on pp. 101, 111 and 271-74.

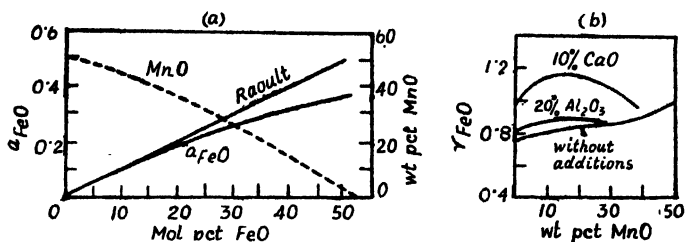


Fig. 4.6—(a) Activity of (FeO) in silica saturated FeO - MnO slag (solid line). Change of FeO with MnO (dotted line). (b) relation of activity coefficient of (FeO) in the same slag. Values with 10% CaO or 20% Al_2O_3 also included. (H. Schenck & G. Wiesner, Archiv f.d. Eisenhuettenwesen, 27, 1956, 5).

Acid slags : Schenck and Wiesner⁵ have determined the activity and activity co-efficient of FeO in SiO_2 -saturated FeO - MnO - SiO_2 slags, which are self-evident from Figs. 4.6(a) and (b). The deviation from R (Raoult's line) is also shown. Fig. 4.6a also shows the change of FeO with MnO in the above slag. The γ -values for slags containing about 10% CaO or 20% Al_2O_3 are also included in Fig. 4.6b. The increase of γ_{FeO} caused by the introduction of 10% CaO is much more than that by 20% Al_2O_3 . In the acid open-hearth it has its importance since lime is sometimes added to increase the boil, caused by the increased activity of (FeO) and the consequent increased carbon reaction. The values are valid for the liquid portions of the slag only.

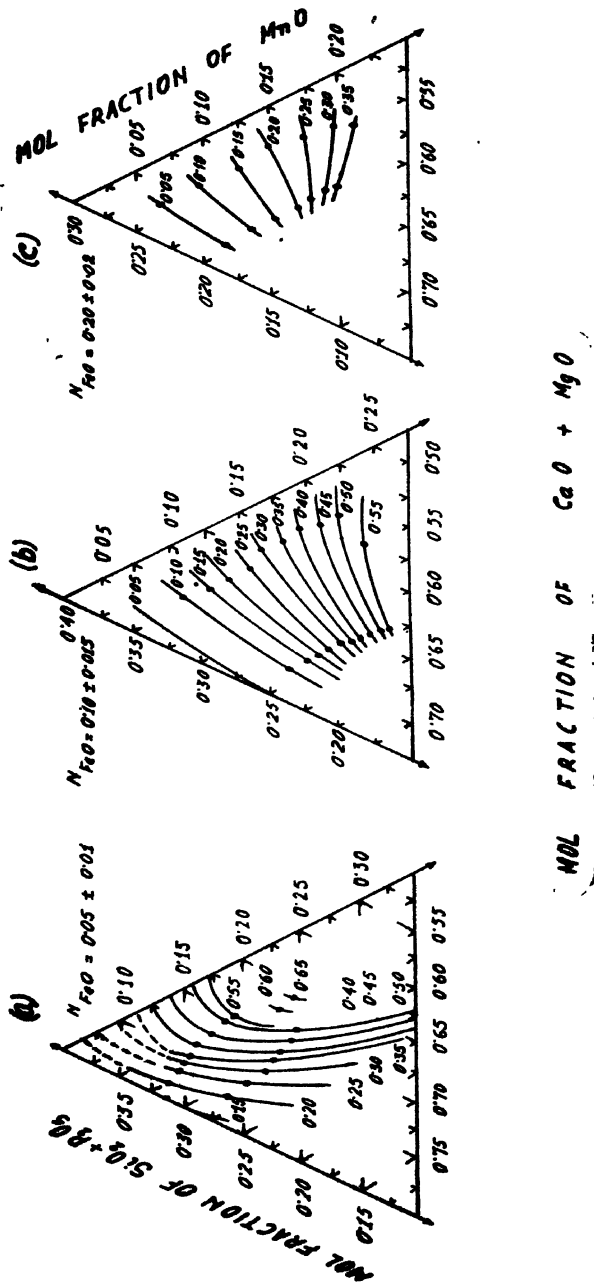


Fig. 4.7—Activity of (MnO) in basic openhearth slags. Base (CaO+MgO), Acid ($SiO_2 + P_2O_5$) in mol fractions. (By courtesy of Iron & Steel Institute).

Activity of MnO

The activity of MnO of any slag can be found out by equilibrating the slag with iron at any given temperature. The manganese reaction is given by Eq. 3.15 from which

$$a_{\text{MnO}} = K_{\text{Mn}} \cdot a_{\text{FeO}} \cdot \%[\text{Mn}] \quad 4.2$$

The value of K_{Mn} at any given temperature is given by Eq. 3.17. It is assumed that K_{M} , which has been derived from experiments with pure FeO-MnO slags, will still be valid for any slag where the (FeO) and (MnO) are defined by their activities and not by their molar concentrations. The values of a_{FeO} can be taken from Fig. 4.4a for basic slags and from Fig. 4.6a for acid slags. Where the slag compositions are such that a_{FeO} cannot be evaluated immediately, the actual oxygen-contents of the metal under such a slag, with the help of Eqs. 3.6 and 3.6a, will furnish the activity values. The activity of MnO has been found to be independent of temperature for all practical purposes.

Basic openhearth slags: The iso-activity curves of MnO are drawn in Fig. 4.7^{10,13} (a), (b) and (c), they being sections at different (FeO)-concentrations, viz: $N_{\text{FeO}} = 0.05, 0.1$ and 0.2 respectively. The total iron content of the slag is calculated as FeO. The range of composition covers more or less the slags of basic steelmaking interest. For any (FeO)-content other than the three given values, a linear interpolation can be resorted to, e.g. if a_{MnO} is required for $N_{\text{FeO}} = 0.07$ and given base and acid values, the activity is found from Fig. 4.7 (a) and (b) for $N_{\text{FeO}} = 0.05$ and 0.1 and then the a_{MnO} for $N_{\text{FeO}} = 0.07$ is simply evaluated (see p. 226).

A close study of the three sections of Fig. 4.7 will show that at given values of N_{base} and N_{MnO} , an increase of FeO (i.e. a simultaneous decrease of N_{acid}) lowers the a_{MnO} ; whereas slags, having higher initial base, show a tendency of increasing a_{MnO} with FeO additions. These diagrams are valid for all temperatures within the steelmaking range.

A comparison of the activity co-efficients of FeO and MnO shows that, with the increase of base, the activity of FeO increases by a much greater extent than the activity of MnO. This indicates a greater stability of Mn-silicates than that of iron.

Acid slag : Fig. 4.8¹⁴ shows the iso-activity curves of MnO on only a portion of the FeO-MnO-SiO₂ ternary diagram, from

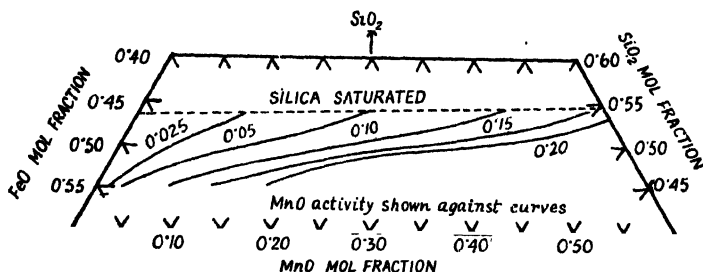


Fig. 4.8—Iso-activity curves of MnO on a portion of FeO-MnO-SiO₂ diagram from the line of silica saturation to N_{SiO_2} of about 0.45. (By courtesy of Iron & Steel Institute).

the line of silica-saturation to about $N_{SiO_2} = 0.45$. A comparison of this figure with Fig. 4.4a brings out the fact that a_{MnO} is reduced, by an increasing acid (SiO₂), to a much greater extent than in the case with a_{FeO} . The cause is the same, that is, the greater stability of manganese silicate. The values, of course, are valid for the liquid portion of the slag only.

Recently, Schenck and Wiesner⁵ have carried out experiments on the manganese reaction with silica-saturated FeO-MnO-SiO₂ slag and the activity and activity co-efficient values derived therefrom are given in Figs.⁵ 4.9(a) and (b). In Fig. 4.9a, the curves show the variations of a_{MnO} at 1540°C in the pure system as well as for slags with 10% CaO and 20% Al₂O₃. The ideal line *R* (Raoult's line) is also shown. The negative deviation of a_{MnO} from ideality is very prominent in all the three cases. It is to be noted here that even the addition of lime gives lower a_{MnO} than corresponding to pure FeO-MnO-SiO₂ slag. This is further clarified in Fig. 4.9b where additions of CaO (and Al₂O₃) give considerably lower values of the activity co-efficient γ_{MnO} than in the pure silicate slag. The cause of such a behaviour is probably due to the ferrous silicate being less stable than the manganese counterpart; the initial addition of a base like CaO releases iron from its silicate (resulting in higher γ_{FeO} , cf. Fig. 4.6), whereupon manganese becomes more stabilised. (See also p. 245).

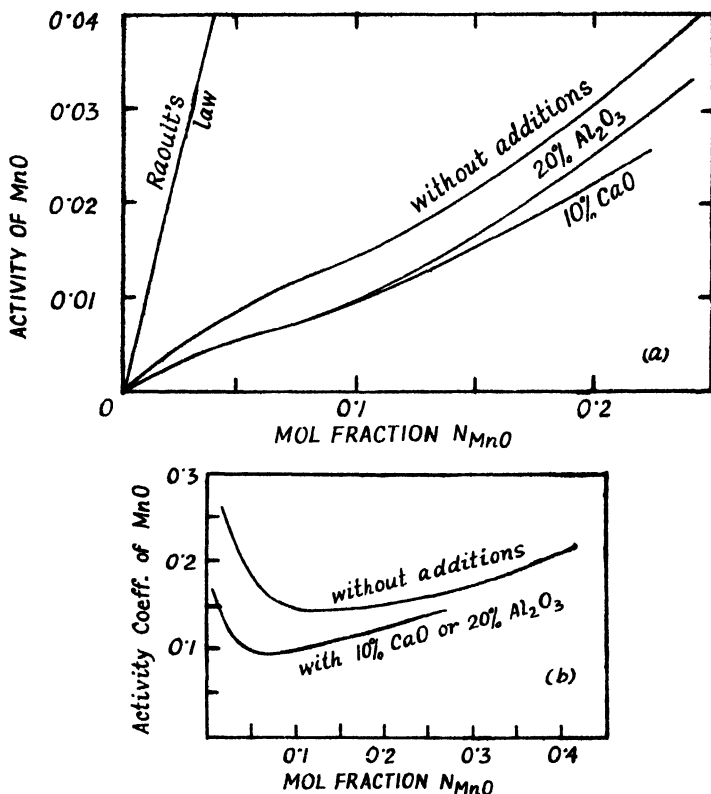


Fig. 4.9—Activity & activity coefficient of MnO in FeO-MnO-SiO₂ slags. (H. Schenck & G. Wiesner, Archiv f.d. Eisenhuettenwesen, 27, 1956, 9).

Activity of CaO

It is difficult to evaluate the activity of lime in complex slags. No reliable data are available. There are some available for simple slags.

Activity of P₂O₅

The activity of P₂O₅ has been determined empirically and discussed on p. 267.

Multiple Slagging¹²

Slag is formed from compounds (insoluble in metal) of both desirable and undesirable elements in steel. The physico-chemical

laws, however, apply equally in both the cases. The amount of any element going over to the slag depends upon the extent of chemical reaction undergone as well as on the total quantity of slag. One of the simple ways of finding the extent of slagging is by the distribution ratio of any element or substance between the slag and the metal :

$$n_x = (x)/[x]$$

where n_x = distribution ratio

$[x]$ and (x) = concentrations of substance x in metal and slag respectively.

Evidently the maximum ratio is given when the system is in equilibrium, i.e.

$$n_{x(\max)} = (x)/[x] \text{ (equilibrium).}$$

Experience shows that the greater the values of $n_{x(\max)}$, the higher is the n_x .

Many steelmaking reactions attain equilibrium and in such cases n_x and $n_{x(\max)}$ are identical. Although the n_x is dependent on the temperature and slag composition, it is not always possible, in practice, to adjust these variables according to one's desire in order to obtain high values of the index n_x . In such cases, either the slag bulk has to be increased or double or multiple slagging resorted to, if a small value of $[x]$ is aimed at. An increase in slag bulk leading to a dilution, induces x to migrate from metal to slag in order to maintain the ratio n_x , based generally on wt. %, constant. The same is true for multiple slagging as well.

The degree of elimination w_x of any substance from the metal to slag is given by

$$w_x = ([x_0] - [x])/[x_0] = 1 - [x]/[x_0] \quad 4.3$$

where $[x_0]$ and $[x]$ are the initial and final contents of x in steel. The per cent elimination is given by

$$W = 100 w_x \quad 4.4$$

$$n_x \text{ is related to Eq. 4.3 by } [x] = [x_0]/(1 + n_x.m) \quad 4.5$$

where m = wt. of slag per unit weight of steel, e.g. slag per ton of steel.

Example : Initial sulphur $[S_0] = 0.06\%$, $n_S = 10$ and $m = 0.15$. From Eq. 4.5, $[S] = 0.024$. Therefore, from Eqs. 4.3 and 4.4, the per cent desulphurisation $W_S = 60\%$. On increasing the slag volume (say, $m = 0.3$), $[S] = 0.015\%$ and $W_S = 75\%$.

It is true, in steelmaking, phosphorus and sulphur can be eliminated to a great extent by increasing the slag volume, yet it has its own inherent difficulties. When n is small, it is advantageous to resort to double or triple slagging for obtaining quality steel. In the basic open-hearth, when the amount of phosphorus in the charge is not very large, it is possible to obtain low [P]-content in steel; but even in such a case, 'flushing' the initial slag and making a new one would protect against the danger of any subsequent rephosphorisation and resulphurisation. In America such a 'flushing' practice is widespread and is carried out during the foaming of slag at the start of refining. In the Thomas, Kaldo and other processes also, the so-called 'fine dephosphorisation' is carried out by changing the initial slag. In the basic electric furnace, the oxidation period is followed by deslagging and subsequent refining with reducing slags.

The success of double or multiple slagging depends upon the amounts of the slag removed and renewed. If it is possible to deslag completely, then the final concentration of x is given by:

$$[x_2] = [x_0] \frac{1}{(n_1.m_1 + 1)(n_2.m_2 + 1)} \quad 4.6$$

n_1 and n_2 are the indices with slags 1 and 2 and m_1 and m_2 the slag bulk in tons per ton of metal.

However, it is practically not possible to run off the entire slag and some slag always remains behind and is incorporated in the renewed slag. If an amount m_1^* is run-off from the 1st slag and the new slag made of amount m_2 , in such a case

$$[x_2] = [x_0] \frac{1 + n_1.(m_1 - m_1^*)}{n_1.m_1 + 1} \cdot \frac{1}{n_2.m_2 + 1} \quad 4.7$$

Example : $[S_0] = 0.06$, $m_1 = 0.15$, $m_1^* = 0.07$, $m_2 = 0.12$, $n_1 = 10$, $n_2 = 15$.

From Eq. 4.7, $[S_2] = 0.015\%$, $W = 75\%$.

Without run-off, from Eq. 4.5, the respective quantities are $[S_1] = 0.024\%$ and $W = 60\%$.

Here, we may consider whether and to what extent the multiple deslagging is useful and necessary. The ratio of the concentrations of $[x]$ after the 1st and 2nd slag is given by :

$$\frac{[x_2]}{[x_1]} = \frac{1 + n_1 \cdot (m_1 - m_1^*)}{1 + n_2 \cdot m_2} = \frac{1 + n_1 \cdot \Delta m_1}{1 + n_2 \cdot m_2} \quad 4.8$$

where $\Delta m_1 = m_1 - m_1^*$, the amount of slag left behind after deslagging.

From Eq. 4.8, we can derive the following conclusions :

- (a) Running-off the slag is unnecessary when $n_1 \cdot \Delta m_1 = n_2 \cdot m_2$, i.e. $[x_2] = [x_1]$.
- (b) Running-off may be resorted to, i.e. $[x_2] < [x_1]$ when $n_1 \cdot \Delta m_1 < n_2 \cdot m_2$.
- (c) Reversion from slag to metal may take place, i.e. $[x_2] > [x_1]$ when $n_1 \cdot \Delta m_1 > n_2 \cdot m_2$.

Ionic Theory of slag^{a,15-19}

It is true that satisfactory equilibrium relations have been obtained by the use of activities instead of molar concentrations in the *LMA* equations. It is, therefore, not necessary to make any arbitrary assumptions about the constitution of slag *vis-a-vis* the slag composition. It is enough to know the change of the activities of the various constituents taking part in the slag-metal reactions with the varying slag compositions. But granting that, for practical purposes a knowledge of the chemical potentials of the various slag constituents is sufficient, yet it is worthwhile to know the fundamental picture of the structure of slag molecules, their constitution and their relations with the slag behaviour so that it is possible to improve the slag technique.

Slags are known to possess electrical properties. The viscosity,²⁰ electric conductance²¹ and electrolysis of the slags prove beyond doubt that they are ionized²² in the liquid state. Crystal

analysis of solid silica shows that silicon occupies the centre of a tetrahedron surrounded by 4 oxygen atoms, one at each of the four corners. The structure of solid substances cannot be expected to undergo, ordinarily, a sudden change on fusion so as to be altogether different from the former solid structure. The transformation from the solid to the liquid state signifies an enlargement of the intermolecular distances accompanying molecular expansion due to thermal agitation. But the co-ordination is expected to remain within a limited distance, as in the solid state, although the configurational regularity of the structure is disturbed. Thus, although the actual geometrical structures of the solid silicate tetrahedra and the liquid silica may vary, their basic features may be expected to resemble each other. Fig. 4.10¹⁹ points to the little change of entropy and, therefore, of disorder of slags on fusion, as is evident from the almost horizontal slope of the free-energy curves.

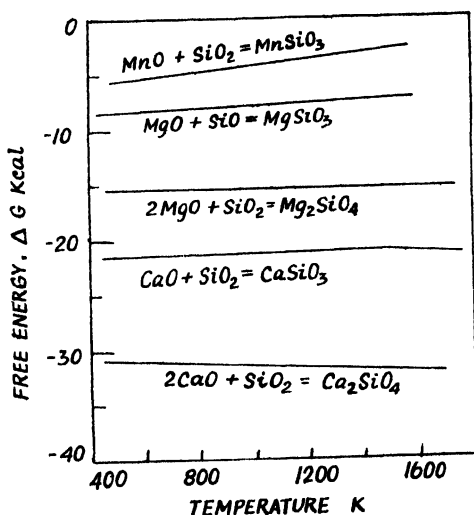
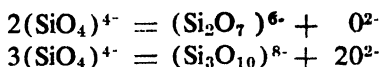


Fig. 4.10—Free energies of formation of some slags.

The $(SiO_4)^{4-}$ or $(PO_4)^{3-}$ ions, which are regarded as individual tetrahedral structures with Si or P at the centre and the oxygen at the four corners, can be assumed to exist also as ions in the complex silicates and phosphates. Silicates, phosphates and also aluminates are co-ordinated tetrahedrally.

When, for example,^{9a,15} CaO enters into combination to form a silicate, two silicon-oxygen bonds are opened up giving rise to Si-O-Ca bond formation, the structure on the whole remaining neutral. As the CaO increases and the orthosilicate $2\text{CaO} \cdot \text{SiO}_2$ is approached, the tetrahedral network gradually breaks down. Due to the entry of Ca^{++} ions in the silicate structure, the electric charge of the molecule becomes unbalanced, since Ca^{++} is much larger than Si^{4+} and the field of electric force naturally comes closer to Si-ions rendering the silicate highly ionized. In the case of phosphorus, whose ions are similar to those of silicon, with more or less identical chemical properties, it is possible for them to interchange their places in the tetrahedra. If it is really possible for P to replace Si, then a relatively acid slag should be able to help in the dephosphorisation; in fact, it has been found to do so to a certain extent. If on the other hand, in place of large cations like calcium, smaller ones like Fe^{++} , Mn^{++} , Mg^{++} are present, they tend to attract the oxygen atoms in the complex more strongly than the Ca^{++} ions do. The density of the negative charge is, therefore, naturally diminished in the periphery, rendering $(\text{SiO}_4)^{4-}$ more easily liable to polymerization;



The polymerization reaction leads to an increase of the oxygen ions. Thus, in an acid slag, it is not possible to estimate correctly the content of the oxygen ions. A correct estimate¹⁵ can be made when the number of calcium ions is more than that of SiO_4^{4-} ions, i.e. when $\text{Ca}^{++}/(\text{SiO}_4)^{4-} > 1$. This ratio covers more or less the entire range of basic open-hearth slags.

Aluminium can enter the tetrahedra as long as its co-ordination number is 4. With high percentage of aluminium, the number is 6 and no longer enters the tetrahedra. Sulphide can replace oxygen and be stabilized, as the positive Ca^{++} ions increase. The ions, which Herasymenko and Speight¹⁵ assumed to be present in basic slags, are

Fe^{2+} , Fe^{3+} , Mn^{2+} , Ca^{2+} , SiO_4^{4-} , PO_4^{3-} , AlO_3^{3-} , O^{2-} , S^{2-} and F^- .

In the basic slags, there is always present an excess of oxygen over that necessary to bind silicon, phosphorus and aluminium to complexes. The tetrahedral structures of silicates and phosphates are stable in an excess of oxygen and, therefore, $(\text{SiO}_4)^{4-}$ and $(\text{PO}_4)^{3-}$ in the basic slags may be considered to be independent simple structural units. The anion AlO_3^{3-} has been assumed to be stable in such slags. The trivalent iron has been assumed to be present as Fe^{3+} . According to Herasymenko,¹⁵ the existence of $\text{Fe}_2\text{O}_5^{4-}$ ions, as suggested by Chipman and Chang,²³ offers no advantage over that of simple Fe^{3+} ions.

In 1938 Herasymenko¹⁶ applied the ionic theory to the slag-metal equilibria. Instead of mol fractions, he used ionic fractions of the slag constituents (number of gm ion of the particular anion or cation divided by the total number of gm ions of anions plus the cations) in the *LMA* equations, for calculating the equilibria. It is improbable, however, that such calculations will give 'constants' for all slag compositions since the ions in slags are not completely disordered and the anions naturally tend to surround the cations and *vice versa*.

Herasymenko and Speight¹⁵ applied the ionic theory to the slag-metal equilibria in the basic open-hearth furnace with considerable agreement to the practical steelmaking data. Their calculation of ion fraction is cited in Table 4.2, the slag analysis being :

48.9% CaO ; 6.7% MgO ; 1.6% MnO ; 9.0% FeO ;
3.3% Fe_2O_3 ; 14.4% SiO_2 ; 13.3% P_2O_5 ; 4.1% Al_2O_3 .

According to Temkin,¹⁷ the slag is completely ionized and each cation is surrounded by anions and *vice versa*. The slag solution, therefore, contains two ionic species both behaving ideally and each species is completely disordered so that one anion position can be replaced by another anion at random. The same applies to cations as well. If in any slag melt Ca^{++} , Fe^{++} , Mn^{++} , Mg^{++} are present, then the ion fraction of say, Mn, will be :

$$\frac{n_{\text{Mn}^{2+}}}{N_{\text{Mn}^{2+}} + n_{\text{Fe}^{2+}} + n_{\text{Ca}^{2+}} + n_{\text{Mg}^{2+}}}$$

where N = ion fraction

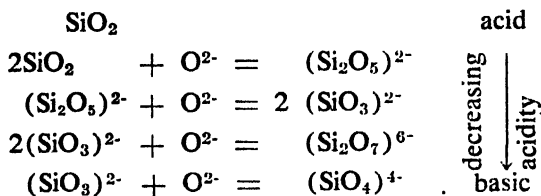
n = number of gm ions

Since the melt behaves ideally, $a_{\text{Mn}^{2+}} = N_{\text{Mn}^{2+}}$

Such propositions of ideality are open to serious objections since it is improbable that the various anions or cations are associated equally with the different oppositely charged ions, irrespective of their size, charge and co-ordination number. The free energies of interactions between the various ions cannot be equal and thus there will be preferential associations between particular pairs of anions and cations whose free energies are comparatively small than the others.

The ionic theory is still limited in its applicability to slag-metal equilibria. It has succeeded in explaining certain reactions *only* under prescribed conditions. It is expected that further work in this regard will establish the theory on a sounder footing.

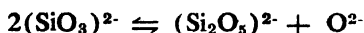
The ionic theory has been profitably applied for explaining the decarburisation in acid open-hearth.²⁴ Chipman and Chang²³ have elaborately discussed the suggestions of G. N. Lewis,²⁵ about the definition of acids and bases. According to Lewis, a base such as oxygen ion O^{2-} is capable of supplying electrons which are available for entry into the valence electron shell of an atom of another molecular species and thereby form a bonded structure. Such a species having such an atom capable of receiving these electrons is defined as an acid. According to this theory, the more basic oxides, e.g. MnO , CaO , in a slag would furnish O^{2-} which can be taken up by any acidic species like SiO_2 . Silica undergoes change in its acidity, as it takes up more and more of oxygen ions from increasing amounts of basic oxides, becoming progressively more basic. The steps are shown below :²⁴



TABLE—4.2¹⁵

Gram ions, N_i	Gram ions of oxygen from metallic oxides	Gram ions of oxygen consumed by anions
$N_{Ca^{++}} = \frac{48.9}{56.1} = 0.8715$	$N_{Ca^{++}} = 0.8715$	
$N_{Mg^{++}} = \frac{6.7}{40.3} = 0.1663$	$N_{Mg^{++}} = 0.1663$	
$N_{Mn^{++}} = \frac{1.6}{70.9} = 0.0226$	$N_{Mn^{++}} = 0.0226$	
$N_{Fe^{++}} = \frac{9.10}{71.8} = 0.1253$	$N_{Fe^{++}} = 0.1253$	
$N_{Fe^{+++}} = \frac{2.3.3}{159.7} = 0.0413$	$3/2 N_{Fe^{+++}} = 0.0619$	
$N_{SiO_2} = \frac{11.4}{60} = 0.2100$		$2 N_{SiO_2} = 0.4800$
$N_{PO_4} = \frac{2.13.3}{112} = 0.1871$		$3/2 N_{PO_4} = 0.2806$
$N_{AlO_3} = \frac{2.1.1}{101.9} = 0.0804$		$3/2 N_{AlO_3} = 0.1206$
	Total : 1.2476 less 0.8812	Total : 0.8812
$N_O = 0.3664$	$N_O \text{ (frc)} = 0.3664$	
Total number of ions $N = 2.1009$		
Ionic fraction N_i/N	$(Ca^{++}) = 0.415$ $(Fe^{+++}) = 0.020$ $(Mg^{++}) = 0.079$ $(SiO_2) = 0.114$ $(Mn^{++}) = 0.011$ $(PO_4) = 0.089$ $(Fe^{++}) = 0.060$ $(AlO_3) = 0.038$ $(O) = 0.174$	

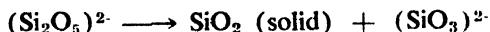
With the normal range of acid slag analysis ($\text{SiO}_2 = 43\text{-}58\%$ and $\text{FeO} + \text{MnO} = 42\text{-}57\%$), it is surmised that the predominant silicate ions in such slags are $(\text{Si}_2\text{O}_5)^{2-}$ and $(\text{SiO}_3)^{2-}$. It is possible that these ions are always present together with those of Fe^{2+} , Mn^{2+} and O^{2-} . It is also assumed that the two silicate ions are in equilibrium :



At high temperatures, the forward reaction is more favoured and, thus, oxygen is released for reaction with carbon in the bath. There occurs a simultaneous migration of Fe (or Mn) to the bath.

It is thought that the basic oxides FeO, MnO, CaO have the same function of supplying oxygen ions to silica to form less acidic silicate ions $(\text{Si}_2\text{O}_5)^{2-}$ and $(\text{SiO}_3)^{2-}$. Since FeO and MnO are almost of the same basic strength, FeO furnishes the excess oxygen if its amount is more than that of MnO; whereas if the amount of the latter is higher, then it supplies the oxygen and Mn migrates to the metal. High MnO slags always show an increase of Mn in the metal during the carbon elimination.

As has been stated on p. 51, the decarburisation velocity decreases if there is a cut back in the fuel or the temperature is reduced or kept constant. This may be because $(\text{Si}_2\text{O}_5)^{2-}$ is less stable at lower temperatures and solid silica is precipitated :



Fitterer²⁴ has used the ionic theory of slag for the explanation of certain phenomena in acid open-hearth steelmaking practice in America. He concludes from the behaviour of the acid open-hearth slags that they probably contain, at all times, at least two silicate ions, $(\text{Si}_2\text{O}_5)^{2-}$ and $(\text{SiO}_3)^{2-}$ together with the oxide or oxygen ions O^{2-} and opposite ions of iron and manganese. Basic oxides like MnO or CaO, when brought in the slag, ionise to give more oxide ions which may either form silicate ions containing more oxygen or themselves react with the metal bath and its constituents. Of the two silicate ions, $(\text{Si}_2\text{O}_5)^{2-}$ is more stable at higher temperatures. Therefore, mere raising of the temperature

will make $(\text{SiO}_3)^{2-}$ to give $(\text{Si}_2\text{O}_5)^{2-}$ and free O^{2-} which increases the carbon removal. If the MnO -content of the slag exceeds 25%, it furnishes the excess O^{2-} needed for the carbon reaction instead of FeO , whose concentration must necessarily be lower since SiO_2 remains more or less constant. As a result, the manganese migrates from the slag to the metal.

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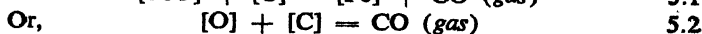
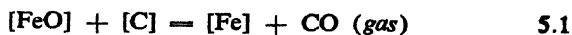
THE REACTIONS AND REMOVAL OF CARBON

General

The oxidation and removal of carbon is one of the most important reactions of steelmaking. Carbon in steel bath reacts with dissolved oxygen or ferrous oxide with the evolution of carbon monoxide. In the pneumatic steelmaking processes, the removal takes place within a few minutes whereas in the open-hearth the time taken is longer and, therefore affects the economy of the furnace. It is said that a minute saved in the production time of a modern open-hearth furnace means a 'cost above' economy of about a pound sterling. The duration of an open-hearth heat depends largely on the time taken for the elimination of carbon to the desired extent and, therefore, the rate of carbon removal has assumed considerable interest to the steelmakers.

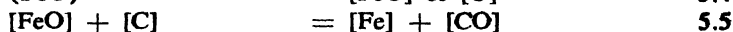
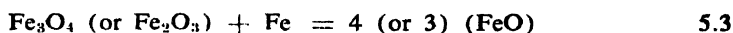
The *boiling* action observed in the open-hearth is due to the evolution of carbon monoxide formed during the carbon removal. The bath obtains its oxygen from the slag and, therefore, the reaction can take place either on the metal-slag interface or in the bath itself. As we will see later, the violent agitation of the bath takes place because of the reaction occurring mainly in the bath itself. This agitation exposes a larger surface of the metal and the slag to the heating furnace gases which enables an easier and speedier transmission of heat by radiation. This movement also enables the entire bath to be heated up by convection. It, further, increases the rate of removal of other metalloids since their removal from the bath to slag occurs mostly on the slag-metal interface requiring easy diffusion and elimination of concentration gradients in the metal and the slag. In fact, without the 'boiling' action and the consequent violent agitation the open-hearth process would have been uneconomical and unsuccessful. The silica roof (m.p. $\sim 1,720^{\circ}\text{C}$) and the steel temperature of $1,600^{\circ}\text{C}$ or more hardly allows about 100°C to play about for heating up the bath. This is impossible without an efficient transmission of heat.

The removal of carbon from the metal probably occurs according to the following equations :



The supply of oxygen or FeO to the bath from slag takes place in part from the open-hearth furnace atmosphere and to some extent from the feed-ore as well. The mechanism of oxidation of the open-hearth metal has already been discussed (*cf.* p. 42). Since the oxygen is mainly supplied by the slag, the *boil* may be stopped or slowed down if this supply is stopped or restricted by the adjustment of slag composition or by other additions. If at any time the iron oxide content of the slag (and of the bath, since they are related by partition coefficient, *cf.* p. 63) is insufficient for a proper carbon boil, high quality iron ore or oxygen gas may be fed to restart or accelerate it by increasing the oxidising power of the slag.

We may assume the following reactions taking place (i) reduction of Fe_2O_3 or Fe_3O_4 in the slag by metal to ferrous oxide which remains in the slag, (ii) the transfer of FeO from the slag to metal, (iii) the reaction between carbon and oxygen (both dissolved in the bath) and the formation of CO (and a little of CO_2) which remains dissolved and, (iv) the evolution of CO dissolved in the bath which is the well-known *boil* :



The final reactions are as given in Eqs. 5.1 and 5.2.

A further source of oxidation of carbon is carbon dioxide which is obtained from the charged lime-stone during *lime-boil*, the equation being



In order to start the carbon reaction the presence of ferrous oxide is required initially. This is obtained by the flame-oxida-

tion of the scrap during the melting down period. (But this ferrous oxide and that obtained subsequently by flame oxidation during the refining period are not sufficient to lower the carbon content to a very great extent and, therefore, the feeding of ore is necessary to supply the excess oxygen for bringing carbon down to the desired level.) The fused metal after melting is not saturated with oxygen as it is not covered with a pure ferrous oxide slag. Ferrous oxide, at first formed, reacts with other products of oxidation like MnO , SiO_2 , etc. as well as with the lime and the hearth lining and thus becomes diluted. This formation of slag restricts the oxidising power of ferrous oxide since the slag, although theoretically capable of absorbing any amount of FeO , remains unsaturated with respect to the oxide. Therefore, according to the partition law, the metal bath which is in contact with the slag remains unsaturated with respect to oxygen. The slag acts as a reservoir for ferrous oxide needed for the oxidation of the metalloids.

In the electric furnaces the atmosphere is not oxidising since aerial oxygen has little access and, therefore, the melting oxidation of the scrap plays a minor role in the supply of the oxidising agent. Here, the slag assumes the entire role for the oxygen supply which is maintained by the addition of ore or lancing of oxygen gas in the bath.

In the pneumatic processes of steelmaking like the bottom or side blown converters, top-blowing of oxygen in the LD. Rotor or Kaldo processes — the oxidation reactions are carried out by aerial or pure oxygen. This oxygen oxidises iron to FeO which reacts partly with the metalloids converting them into their oxides, and partly goes to the slag.

The carbon elimination reaction given by Eq. 5.1 is obtained from the overall reactions Eqs. 5.4-5.6. Now, in any multi-phase heterogeneous reaction, the overall velocity is determined by the speed of the slowest of the individual reactions. If it is assumed that reactions 5.3 and 5.4 are fast enough to maintain adequate supply of FeO required in Eq. 5.5 and that the conditions for the formation of the new gaseous phase CO are favourable, then the reaction 5.5 should determine the velocity of the reaction 5.1. With these assumptions Herty¹ and Schenck, Riess and Brügg-

mann² propounded the following equation for carbon elimination in normal open-hearth operations :

$$-dC/dt = v = k_1 \cdot [\text{FeO}] \cdot [\text{C}] - k_2 \cdot p_{\text{CO}} \quad 5.8$$

where

$-dC/dt = v$ = decrease of carbon in bath in unit time, i.e. rate of decarburisation measured in %C/minute.

$[\text{FeO}]$ and $[\text{C}]$ = respective concentrations in metal bath.
 p_{CO} = the total pressure of rising CO gas bubbles

which must overcome the atmospheric and ferrostatic pressures of metal and slag. (Schenck³ calculated that in open-hearth, neglecting the slight amount of N_2 and H_2 , the $p_{\text{CO}} = 1.1$ atm and in Bessemer converter $p_{\text{CO}} = 0.45$ atm).

k_1 and k_2 = velocity constants of the forward and reverse reactions of Eq. 5.1 respectively. Schenck *et al*² found that both in acid and basic open-hearths these constants are independent of temperature and composition of the lining but vary with the carbon content.

Schenck assumed that this reaction between the carbon and oxygen dissolved in steel bath was rate-determining and on the further assumption that $[\text{FeO}]$ was proportional to free-(FeO) of slag, he laboriously calculated a series of curves which enable one to find out the iron content and the basicity of open-hearth slags, at given carbon contents and temperatures, required for various rates of decarburisation.³ He also derived curves for finding out the oxygen content of steel bath from various rates of decarburisation (*cf.* Fig. 10.2).

Schenck has shown that the observed decarburisation curves in open-hearths compare favourably with those calculated by his method. But his theory of carbon removal, where reaction 5.1 is

inherently very slow,^{4,5} has met with strong objections. Doubts have also been expressed regarding the validity of Eq. 5.8 for the calculation of oxygen content of steel from the rate of decarburisation.

The decarburisation velocity in open-hearth is of the order of 0.05 - 0.1% C/h in a normal steady boil and about 0.6 - 0.7% C/h after heavy ore additions. This is extremely slow compared to the same reactions in the Bessemer converters where about 3.5 %C is blown away in about a quarter of an hour or in the open-hearth itself where the carbon reaction takes place almost with explosive violence when pig iron is added to a highly oxidised scrap. Further, according to Goodeve,⁶ ordinary homogeneous chemical reactions, like the one between oxygen and carbon in liquid steel as envisaged by Schenck, should have extremely high velocity at steelmaking temperatures unless the activation energy is very high of an order greater than 100 Kcal/gm mol, which is normally rather rare. Vallet⁷ has calculated that the apparent activation energy of the [C]—[O] reaction is approximately 28 Kcal/gm mol and such a low value indicates the reaction velocity to be immeasurably fast at steelmaking temperatures. The slow decarburisation, therefore, is presumably controlled by the rates of diffusion of the constituents and chemical kinetics cannot be the rate controlling factor. Again, Schenck did not assume the difficulties of bubble formation which is opposed by surface tension forces as we will see presently. According to Ranque,⁸ a CO-evolution pressure of about 55 atm will be necessary for the nucleation of a bubble in liquid steel. If any bubble is formed in the metal, it would dissolve unless its diameter is large enough as explained later.

Schenck's application of mass law equations for decarburisation should predict a direct relationship between the excess of the reactants and the rate of carbon elimination (*cf.* Eq. 5.8) but various investigators^{12,9} obtained indifferent results. As early as 1935, Körber and Oelsen⁹ raised their objection to the application of mass law equation because, in their experiments with C- and O-containing liquid steel in small smooth glazed crucibles under FeO-MnO-SiO₂ slag, they could hold down 20-30 times the equilibrium carbon content for a definite amount of oxygen without the sample showing signs of a 'boil'. Boiling started when the

melt was stirred with solid iron rod or when the crucible wall was scratched. With a crucible having rough unglazed wall, the 'boil' started in the presence of much less carbon. Taking Vacher and Hamilton's constant¹³ at 1,600°C (*cf.* p. 66), the decarburisation should run as long as $[C] \cdot [O] > 0.0025$. Körber and Oelsen conclude that decarburisation rate is dependent on physical rather than on chemical processes. They presume that Eq. 5.6, which concerns the evolution of dissolved CO as a gaseous phase, is the rate-controlling step. It is a sort of evaporation process which can take place if the evolution pressure p_e is greater than the partial pressure p_a of carbon monoxide in any gas phase in contact with the bath. Thus the velocity of evaporation will be greater, the greater the p_e and the less the p_a and the greater the surface area of the bath in contact with the gas phase. They have derived an equation for decarburisation similar to that of Schenck but containing a factor s which is the surface per unit weight of melt at the disposal for evaporation at the moment :

$$-dC/dt = k_1 \{ k_2 \cdot [\text{FeO}] \cdot [C] - p_a \} s \quad 5.9$$

According to the above equation the velocity of chemical reaction between [FeO] and [C] is not the same as velocity of decarburisation but is determined by the physical process of separation of CO gas from the melt. It is difficult for CO to form a bubble inside the liquid metal even at high concentrations of [O] and [C] since any small bubble at first formed will be under such a heavy capillary pressure (as explained later) of the surrounding melt that the evolution pressure cannot overcome it. A bubble of sufficient diameter will become stable when the capillary pressure is less than the evolution pressure for given [O] and [C] contents. Since the available surface is very rarely sufficient for spontaneous evolution of CO, such surface is presented by porous materials like ore or other additions from outside or by the cracks and crevices at the bottom of the open-hearth furnace (such vacant places are not reached by liquid iron because of its surface tension forces) or by any earlier formed CO gas bubble itself or by other gases passed through the melt, e.g. air in bottom- or side-blown

converters. Such a phenomenon is possible because the product of the reaction is gaseous and also dependent upon pressure.

Körber and Oelsen,⁹ after considering the problem from various aspects, have reached the following conclusions :

(a) decarburisation can proceed *only* if $k_2 \cdot [\text{FeO}] \cdot [\text{C}] > p_a$

(b) even if (a) is satisfied, the decarburisation, i.e. CO evolution may not take place if the necessary surface is not available, i.e. if surface s is zero, the velocity will naturally be zero. The velocity will change with s , notwithstanding $[\text{FeO}]$, $[\text{C}]$ and p_a remaining constant. If s is

large, then the velocity will also be large even if $(k_2 \cdot [\text{FeO}] \cdot [\text{C}] - p_a)$ is small. With rising velocity, the available

free surface increases, which in its turn increases the velocity still more (the reaction becoming autocatalytic). Thus, an increase in velocity does not always signify a rise in $[\text{FeO}]$ and, therefore, contrary to Schenck's theory, a definite relationship between $[\text{FeO}]$ and the velocity of decarburisation should not exist. (Since Schenck has calculated the velocity constants from works data, it is possible that his formula includes the physical process of CO evolution.) From the equilibrium relationship $p_a = k_2 \cdot$

$[\text{C}] \cdot [\text{FeO}]$ and $[\text{FeO}]/(\text{FeO}) = L'$, the condition for decarburisation at any moment is as follows :

$$p_a / k_2 \cdot [\text{C}] < [\text{FeO}] < L' \cdot (\text{FeO}) \quad 5.10$$

Now, in the open-hearth process, until carbon becomes very small, the state of bath oxidation is controlled chiefly by the element. Therefore, the lower limit of $[\text{FeO}]$ is determined by $[\text{C}]$ and p_a ; the upper, by the (FeO) content of liquid slag and the temperature. The difference between the upper and lower limits represents the driving force of the decarburisation reaction. As the difference becomes smaller, the velocity will become less and less which can be increased by raising the $L' \cdot (\text{FeO})$, e.g. by the addition of ore or increasing the temperature. Both these factors must be increased in order to arrive at a low C-content. No decarburisation is possible when these upper and lower limits correspond together.

where the concentration of oxygen is the highest in the bath, could not be entertained because, if it is so, then the concentrations of other dissolved elements will be higher in the lower portions than in the upper portions of the bath where these elements will be easily oxidised due to the higher [O]-concentrations (since the lower layer will not be in equilibrium with the slag). Also, if it is so, then the 'boil' will be confined to the upper portions and the lower layer will naturally be cold. But Larsen finds that the Mn-, P-, S-, C-contents and the temperature are almost the same in the upper and lower portions. Therefore, it is presumed that the bubbles are formed on the lining and the hearth of the furnace from where they rise, growing bigger during their passage upwards through the bath by incorporating more of CO and thus creating a turbulence which equalises the temperature and the concentrations of the dissolved elements throughout the bath. The velocity of carbon reaction will depend upon the physical conditions of the hearth which facilitate bubble formation as well as on how fast the delivery of O and C to very near the hearth surface could be maintained.

It is surmised that the holes or crevices on the hearth or in the additions of charges like ore, scrap, lime, during the refining serve as focal points for the formation of bubbles. Richardson¹⁷ indicates that, for any CO-bubble to form, its minimum evolution pressure P_E must be equal to $p_{CO} = (1 \text{ atm.} + p_f + 2\sigma/r)$ where p_f is the ferrostatic pressure at the place of bubble formation, i.e. at the hearth surface, σ the surface tension of steel and r the radius of the crevice. Therefore, the minimum [C].[O] product necessary to enable bubble formation at the hearth crevices will be that in equilibrium with P_E . It has been shown that the product will have to be twice its equilibrium value (i.e. $2m$; for m , see Eq. 3.10) before any bubble could form in a crevice of 0.008 cm. diameter and at a bath depth of 40 cm. This explains why an 'excess' oxygen, i.e. $\Delta[O]$, is necessary for the 'boiling' action. But one can conclude as well that as carbon increases, the minimum value of $\Delta[O]$ necessary for the maintenance of a boil (hearth and other conditions remaining the same) should decrease which is, however, contrary to the findings of Larsen, according to whom, $\Delta[O]$ is independent of [C].

Further evidence of the possibility of bubbles nucleating in the holes and crevices of the hearth is apparent from the findings of Brower and Larsen¹⁸ that $\Delta[\text{O}]$ is higher in new or fettled furnaces, whereas it is lower in old rough unfettled hearths since the number of crevices are higher in the comparatively rough surface which may facilitate the nucleation of bubbles. They have also found that the C and O contents of the samples taken from the bottom of the bath are such that the m -values are much nearer to equilibrium than is the case at the upper portions of the bath. According to Leiber,¹¹ the $[\text{O}]$ concentration is not uniform throughout the bath but is lowest near the hearth.

The natural conclusion from what has been said above is that the carbon reaction and, therefore, the factor controlling the rate of decarburisation is governed by the formation of CO bubbles. The excess oxygen ΔO is supposed to be due to the excess pressure caused by the forces of surface-tension and ferrostatic pressure of the metal and slag column above the hearth. On this assumption, Vallet⁷ has calculated the radius of gas bubbles in equilibrium with the metal as

$$r = \frac{9 \cdot 87 \cdot 10^{-7} \cdot 2 m_{\sigma}}{\%[\text{C}] \cdot \Delta[\text{O}] - m p_f} \quad 5.11$$

[This has been derived from Eq. 3.10 and p_{CO} on p. 188 on the assumption that $\Delta[\text{O}]$ is due to the ferrostatic and surface-tension forces, from where it follows :

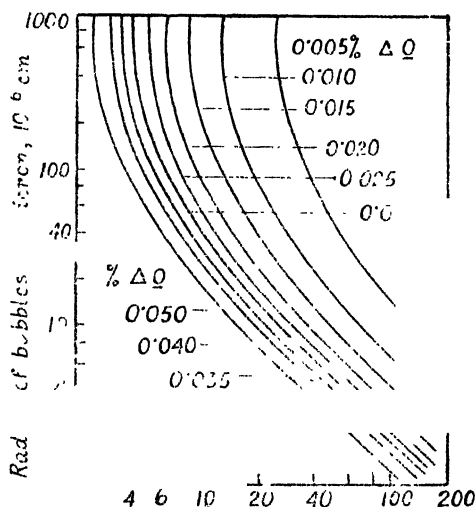
$$\Delta[\text{O}] = \frac{m}{\%[\text{C}]} \left(p_f + 9 \cdot 87 \cdot 10^{-7} \cdot 2 \frac{\sigma}{r} \right) \quad 5.12$$

It follows from the above equation that in a shallow bath where p_f is very small, the radius of the bubble varies inversely with $\Delta[\text{O}]$ or $\%[\text{C}]$ when either of them is kept constant. In deeper baths the ferrostatic and surface tension forces come into play and for a stable bubble,

$$\Delta[\text{O}] > m p_f / \%[\text{C}]$$

Since m is constant (0.0022% at 1600°C),¹² it follows that $\Delta[\text{O}]$ is directly proportional to p_f , i.e. bath depth, and inversely to the carbon content of the bath. As for example, if $p_f = 0.5$ atm. (bath depth $h = 70$ cm.) $m = 0.0022$ and $\% [\text{C}] = 0.05$, it is necessary, for bubble to exist, that $\Delta[\text{O}] > 0.022\%$. For same $[\text{C}]$ and $h = 40$ cm, $\Delta[\text{O}] > 0.013$.

From the above considerations, Vallet has drawn Fig. 5.2 which shows the variation of radius r of the bubbles in equilibrium with the metal containing various amounts of carbon and $\Delta[\text{O}]$ at $1,600^\circ\text{C}$ and ferrostatic pressure of 0.5 atm.



[$\Delta[\text{O}]$ denotes excess oxygen in steel.]

Fig. 5.2—Variation of the radii of the bubbles in equilibrium with the metal at $1,600^\circ\text{C}$. and ferrostatic pressure of 0.5 atm., as a function of carbon content for different values of excess oxygen $\Delta[\text{O}]$.

(By courtesy of Iron & Steel).

Carbon monoxide bubbles cannot form spontaneously in the metal because the supersaturation with oxygen necessary for the purpose is not possible to attain. Bubbles may, however, form at the pores and holes of the hearth, lump ore, lime or other additions if their radii of curvature are higher than that given in Fig. 5.2. The C and O reacting in the metal can then form CO gas

at the gas-metal interface, join the gas present at the pores and continue to grow until, when large enough, they detach themselves and come up as bubbles.

The minimum radius of curvature for bubble formation increases as the carbon content decreases during decarburisation provided $\Delta[\text{O}]$ remains constant. Therefore, as the carbon removal proceeds, the pores will gradually stop functioning as nuclei for bubble formation, the smaller ones being the first to do so. In order that all the pores should function, $\Delta[\text{O}]$ has to rise as $[\text{C}]$ decreases. Such an increase of $\Delta[\text{O}]$ may be effected by the addition of iron ore which brings smaller and, therefore, more cavities into operation for bubble formation; it also itself brings with it more pores and holes which serve as further sources of nucleation and, being present on the surface of the bath, are almost free from the restrictive forces of ferrostatic pressure. The CO_2 evolved from limestone is a further source of gas bubbles, into which CO from the carbon reaction can escape, thus facilitating carbon removal. This would lead to the decrease of $\Delta[\text{O}]$ although, theoretically, $\Delta[\text{O}]$ should increase because CO_2 is an oxidising agent and reacts with C to form CO. Eq. 5.11 gives the minimum equilibrium radius of bubbles. If this value is exceeded, the bubble will no longer be in equilibrium under the same conditions. Therefore, the bubbles can receive more CO from the carbon reaction around the bubble-metal interface. As the bubbles grow larger, they are able to take more and more of C(). The reaction thus becomes auto-catalytic.

It is clear that the area of the bubble surface becomes important in decarburisation. Vallet has deduced theoretically the rate of decarburisation as a function of surface area s , $[\text{C}]$ and $[\text{O}]$ -contents :

$$-d\%[\text{C}]/dt = K.s. \%[\text{C}].\Delta[\text{O}] \quad 5.13$$

The equation shows that the decarburising rate increases with the increase of total surface area and/or $\Delta[\text{O}]$. The surface area cannot be altered at will to a great extent, but $\Delta[\text{O}]$ may be easily changed by ore additions. Since the increase in $\Delta[\text{O}]$ brings into play smaller, formerly non-functioning cavities, the surface area s also increases, thereby increasing the decarburisa-

tion rate, proportionately more than expected by a certain increase in $\Delta[\text{O}]$.

This increase of decarburisation rate will consume more oxygen and bring down $\Delta[\text{O}]$. If the rate of supply of oxygen is diminished (by suitably adjusting the slag), the $\Delta[\text{O}]$ decreases, thereby causing stoppage of smaller cavities from functioning which, in its turn, decreases the bubble surface area and therefore, the decarburisation rate and oxygen consumption, resulting in a slowing down of the decrease of $\Delta[\text{O}]$. This mechanism probably helps to keep $\Delta[\text{O}]$ more or less constant (except after newly made additions) in the bath which has been found to be the case by Larsen in normal practice.

Darken¹⁹ suggests the following expression for the explanation of $\Delta[\text{O}]$:

$$\Delta[\text{O}] \propto \frac{\text{slag-metal interfacial area}}{\text{gas-metal interfacial area}} \cdot \Delta[\text{O}']$$

where $\Delta[\text{O}'] = \%[\text{O}]$ (equilibrium with slag) — $\%[\text{O}]$ (actual). This expression also indicates that $\Delta[\text{O}]$ should increase during the ore-boil because of increase of $\Delta[\text{O}']$ and that $\Delta[\text{O}]$ should decrease during the lime-boil because of greater bubble- or gas-metal interfacial area.

The value of the product $K.s.$ obtained by Vallet is comparable with Schenck's constants (Eq. 5.8). It is, therefore, not surprising that Schenck's equation of decarburisation rate, although theoretically untenable, is useful for practical purposes at least in the lower range of $[\text{C}]$ -contents.

Mackenzie and Urie²⁰ have criticised the hypothesis of bubble formation being the slowest step in the decarburisation reaction because of variations in the oxygen-contents and the rates of decarburisation from cast to cast. Such a hypothesis also demands that oxygen in steel should reach equilibrium with slag. If diffusion is assumed to be the slowest step, then evidently $\Delta[\text{O}]$ should be zero.

As we know, oxygen must be supplied to the metal by the slag continuously in order to burn the carbon and maintain an excess oxygen. Except at low carbon, the oxygen in metal is

never sufficient to remove the entire carbon. Darken^{19,21} assumes that the overall rate of carbon elimination depends upon two slow steps (i) diffusion of oxygen through a thin dead film of metal of the order of 0.003 cm. in contact with slag; (ii) diffusion of oxygen through a similar film on the bubble-metal interface. He derived the equation for the rate of decarburisation

$$-\frac{d[C]}{dt} = D \frac{\Delta[O']}{l \Delta l} \frac{12}{16}$$

where Δl and l are the film thickness and bath depth and D the diffusivity of oxygen. The two rates of decarburisation calculated from the above, i.e. 0.67% C/h and 0.14% C/h during heavy oreing and normal boil respectively, agree well with those observed in practice.

Basic Open-hearth

The modern theories of decarburisation in open-hearth may differ from that of Schenck, but latter's work in this field remains still the most exhaustive and of great practical utility. Schenck's decarburisation Eq. 5.8. shows that the rate of carbon elimination V (% [C] per min. or per hour) at any given temperature increases with the *free* (FeO) of slag and [C]-content of metal. Again, for a metal with a given [C] under a slag with constant free (FeO), the carbon elimination increases with temperature since the partition coefficient $L_{FeO} = (FeO)/[FeO]$ and the free (FeO) itself rise with increase of temperature.

Fig. 5.3³ shows the relation between [C] and free (FeO) for $V = 0.006\%$ C/min. and $V = 0$, i.e. at the equilibrium at different temperatures. The significance of $V = 0$ is that the carbon reaction has come to a standstill, i.e. the bath is 'off boil'. In order to obtain or maintain a boil it is imperative that free (FeO) must be higher than that corresponding to equilibrium. Fig. 5.3 draws out clearly that the slag must contain a larger amount of (FeO) than that corresponding to equilibrium if the boil has to be maintained at $V = 0.006$. At higher temperatures the required amounts of (FeO) are evidently much less in both the cases.

It may be mentioned here that only the free (FeO) has been taken into consideration in the above and, therefore, the arguments are applicable to both basic and acid open-hearths. Since

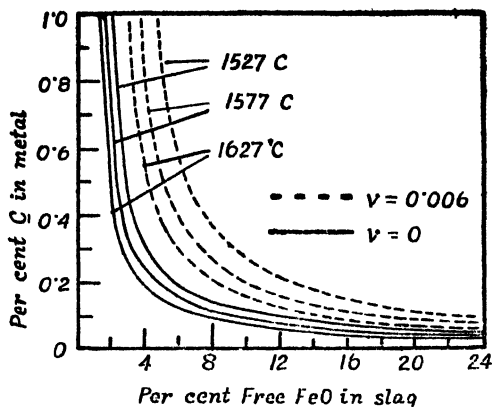


Fig. 5.3—Relation between free ferrous oxide of openhearth slag and carbon content of steel at 1,527, 1,577 & 1,627°C, for rates of decarburisation $V=0$ and $V=0.006$ % C/min. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck.)

free (FeO) is obtainable from the total compositions of acid and basic slags, the course of decarburisation can be easily studied.

Schenck has drawn, with the help of free (FeO) charts and Eq. 5.8, figures relating C-content of metal and total iron content (Σ Fe) with varying silica and lime contents of the slag at different decarburisation rates, $V = 0$, $V = 0.003$ and $V = 0.006$ % C/min, at temperatures of 1,527° and 1,627°C. In each category there are two cases, one with $\Sigma \text{SiO}_2 + \Sigma \text{CaO}' = 50\%$ and another $\Sigma \text{SiO}_2 + \Sigma \text{CaO}' = 60\%$. ($\Sigma \text{CaO}' = \Sigma \text{CaO} - 1.57 \Sigma \text{P}_2\text{O}_5$).

Fig. 5.4 shows the relations at equilibrium, $V=0$. Here (Σ Fe) represents the minimum iron content of slag required to attain a given [C]-content when the bath is quiet or 'off boil'. We can see from the figure that :

- (1) (Σ Fe) of slag (which denotes iron present in oxidised form only) rises as [C] decreases.
- (2) (Σ Fe) varies considerably with the lime and silica contents at a given temperature. For each [C]-content, there is a minimum (Σ Fe) in the curves.

- (3) (ΣFe) needed, for attaining a given $[\text{C}]$ -content, decreases with increasing temperature.
- (4) Influence of increasing MnO on decarburisation is negligible (not shown in the figure).

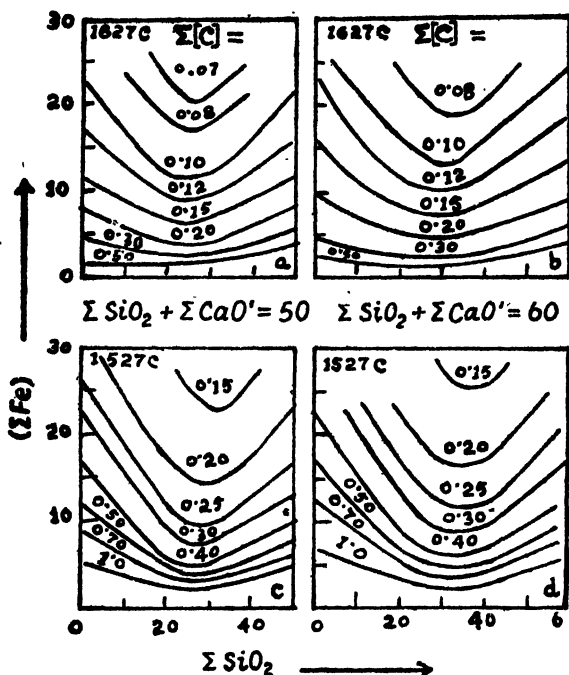


Fig. 5.4—Relation between the total iron content of openhearth slag and its lime & silica contents, when in equilibrium ($V=0$) with steel of various carbon contents, valid for $(\text{MnO})=10\%$. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

Fig. 5.4 corresponds, as already stated, to a bath at equilibrium or 'off the boil'. Fig. 5.5 shows the same relationship as in Fig. 5.4 but at different rates of decarburisation, $V=0.003$ and $V=0.006\%$ C/min. The qualitative nature of the curves in the two figures is the same but the (ΣFe) -requirement of the slag increases, other conditions remaining the same, for achieving higher rates of decarburisation.

If it is intended to restart the boil in a quiet bath or to increase the velocity of carbon removal, it is necessary to increase

- (a) total iron content of slag
- (b) lime (ΣCaO)' and silica (ΣSiO_2) contents of slag
- (c) rate of decarburisation, V
- (d) carbon content of the metal, $[\text{C}]$
- (e) temperature.

These points are discussed briefly below³ :

(a) Total iron content (ΣFe) is the amount of oxidised iron present in slag in weight per cent. The actual weight varies according to the slag volume. The laws of chemical equilibrium deal with the concentration and not with amounts by weight. This (ΣFe) varies during the furnace operation and it is higher :

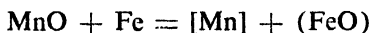
- (1) the higher the rate of decarburisation
- (2) the lower the C-content of metal
- (3) the higher the $(\text{CaO})'/\text{SiO}_2$ ratio
- (4) the lower the temperature.

All these are very apparent from Figs. 5.4 & 5.5. Higher decarburisation rate needs greater amount of oxygen for the reaction and, other conditions remaining the same, the activity of iron oxide in slag has to be raised, which is only possible by increasing the iron content of slag (see Fig. 4.5). Similar is the case if lower carbon content is desired, since low- $[\text{C}]$ is in equilibrium with high $[\text{O}]$ and needs maintaining a high iron oxide activity in the slag. As regards the lime-silica ratio, the Fig. 4.5 shows that as the ratio increases, the (FeO) -activity decreases for the same iron-content; and if the activity has to remain unchanged, it is necessary to increase the (Fe) -content as the ratio increases. Lower temperature needs higher (FeO) -activity since the supply of oxygen to the bath is lowered, as can be seen from the relation $\%[\text{O}] = a_{\text{FeO}} \%[\text{O}]_{\text{max}}$ ($[\text{O}]_{\text{max}}$ decreases with decreasing temperature, cf. Eq. 3.6). It may be noted here that Back,²² Sonntag and Wark,²³ and others observed the increase in iron oxidation with increasing $V = (\Sigma \text{CaO})/(\Sigma \text{SiO}_2)$ ratio; and Kuhn²⁴ observed low iron contents of slag in very hot melts.

From a purely physico-chemical point of view, it is immaterial for the course of carbon reaction *vis-à-vis* iron-content of slag by

which method it is supplied to the slag. The build-up of (Σ Fe) may be either by the iron oxides (rust) in the scrap, flame oxidation during melting, oxidation of bath by slag or directly by the addition of ore, mill-scale, etc. Other factors remaining constant, the need to add ore or scale will be more or less according to the extent of the initial oxide content in the charge and the flame oxidation. In selecting ores for additions, its silica and lime contents must be taken into account. Larger amounts of the former may deteriorate the dephosphorisation and desulphurisation, while that of the latter may lower the oxygen potential. In either case, it may necessitate addition of lime or sand respectively, which would increase the slag bulk. Since a minimum (Σ Fe) concentration is necessary for a desired [C]-content, an increase in slag bulk would lead to a greater iron loss (of course, some iron will be recovered from the added ore by reduction).

It is sometimes the practice, in order to introduce metallic Mn in the bath, that manganese ore is used in addition to iron ore to carry out carbon oxidation. Since the higher oxide Mn_3O_4 is almost quantitatively reduced by iron to form MnO and FeO, we consider the reaction of MnO with the metal :



In both the reactions, FeO is formed which is distributed between the slag and the metal according to the partition coefficient. Thereby, the (Σ Fe) of slag is increased by a certain amount which affects the decarburisation in the same way as does the addition of iron ore. The reaction above, is endothermic and proceeds to the right with increasing temperature and, therefore, the decarburising action of manganese ore is more effective at high temperatures.

(b) The effect of lime and silica on the FeO activity in basic slags is shown in Fig. 4.5. In the range of basic steelmaking slags, the FeO activity decreases, for a given total iron content of slag, as the lime/silica ratio increases. The importance of lime and silica contents in the basic open-hearth has been dealt with under (a) and (c) of this section. At $\text{CaO/SiO}_2 \sim 2.7$, the (FeO)-activity is maximum for any given (Σ Fe). Therefore, other conditions remaining the same, this basicity should exhibit

the maximum decarburisation rate. As a corollary, for any given rate of decarburisation, the (Σ Fe) will be the minimum as the slag approaches a basicity of 2.7. Below this basicity an increasing amount of lime and above it, an increasing amount of silica would accelerate decarburisation.

(c) The rate of decarburisation V in the basic open-hearth processes increases :

- (1) with increasing (Σ Fe) of slag
- (2) with increasing [C]-content
- (3) with decreasing $(\text{CaO})'/(\text{SiO}_2)$ ratio
- (4) with increasing temperature.

Again, all the above points are apparent from Figs. 5.4 & 5.5. These figures are derived from Eq. 5.8 on the assumption of the applicability of the law of mass action. Although the present ideas of the mechanism of carbon reaction envisage the rate of bubble formation (and also oxygen diffusion) to be the deciding factors in the rate of decarburisation, nevertheless, Schenck's formulations have wide practical applicability since they are based on a mass of actual steelmaking data. The ease of bubble formation and diffusion of oxygen (fluid slag and enough turbulence) should and do affect the decarburisation rate. From p. 190, it is clear that a deep bath would need more $\Delta[\text{O}]$ than a shallow one and, therefore, for a given slag with a given (Σ Fe) or (FeO)-activity, the rate of decarburisation will be slower.

The influence of factors (1), (2) and (4) is evident from what has been said under (a). Decrease of $(\text{CaO})'/(\text{SiO}_2)$, for given iron-content, increases the FeO-activity in the range of basic open-hearth slags (Fig. 4.5) and, therefore, increases V by raising the oxidation potential of the bath.

*Foaming of slag*²⁵⁻²⁸

It has been the frequent experience of steel melters in open-hearths, especially in basic open-hearth furnaces, that the slag *foams* or *bulges up* because of entrapped gas bubbles. Such a foaming slag acts as a sort of insulating layer, seriously hampering the transfer of heat from the heating gases to the bath. This entails considerable delay in the furnace operation and the refining is prolonged with the consequent losses and disadvantages.

Foaming generally occurs when the charge contains excessive silicon or melts cold or the flame is non-luminous when fired with fuels like coke-oven or natural gases. The bubbles, it is presumed, are formed by CO which is evolved during the carbon and oxygen reaction but held by the slag during its passage through the slag. According to Larsen,²⁶ it is possible for H_2O and CO_2 in the furnace gases to react with metal surface and form CO and H_2 . Since the foam is caused only by very small entrapped bubbles, it is to be expected that they are evolved in or near the metal surface and, therefore, do not grow large. Although the carbon and oxygen reaction needs sufficient nuclei for CO to evolve, the excess oxygen supplied by the slag to the metal at the slag/metal interface and the solid slag particles at the same interface may facilitate CO evolution. It is doubtful that the main carbon reaction, which occurs at or near the hearth, should cause foam. Since the CO bubbles during their passage through the bath grow large enough, it is improbable that they are caught in the slag and cause foam.

As soon as the signs of foam are visible, the melter takes immediate steps to counter-act it. The usual measures are :

- (i) increase of the firing rate and directing of flame towards the bath ;
- (ii) increase of tar to obtain luminous flame ;
- (iii) addition of lime to the slag.

How and why these above measures help to control foaming will be clear when we consider the causes which stabilise the bubbles in the slag. One of them is naturally the viscosity of the slag. If the bubble-wall is surrounded by a viscous material, the bubble would be unable to rise up or burst out. When viscosity is reduced, as for example, by additions of burnt lime and scale which liquefy the slag, the foaming is largely eliminated. According to Marsh,²⁰ the temperature plays an important role which is substantiated by the fact that, at low temperatures, the usually non-foaming lime-rich slags could be made to foam. This suggestion, however, is not opposed to the high viscosity theory since a decreasing temperature increases the viscosity.

Although viscous slags do cause foaming, it has been found that even very fluid slags are not immune to such troubles. Foaming in the basic open-hearth, generally, occurs with low-lime, FeO- and silica-rich slags which are very fluid. The cause in such cases has been traced to the stability of bubbles on account of the surface tension forces. Since pure liquids seldom foam even if their surface tension is low, it is surmised that dissolved surface-active substances form an adsorption layer which is capable of lowering the liquid/gas interfacial tension. This adsorption layer should, however, be viscous and strong enough to stabilise the foam. In basic open-hearth, the first slag when the boil begins, is low in P_2O_5 and CaO and under such circumstances silica is the only constituent which can lower the surface tension of liquid FeO. It is probable, the silica-rich adsorption film stabilises the bubble.

(d) The carbon content at which a bath may be quiet (equilibrium) depends mainly upon the slag composition and the temperature. A minimum carbon content can be achieved by :

- (1) high (Σ Fe) of slag
- (2) low $(CaO)/(SiO_2)$ ratio
- (3) low rate of decarburisation at the end of refining
- (4) high temperature.

The factors (1), (2) and (4) are readily understandable since they increase the oxidation potential of the bath and the slag. Low rate of decarburisation is necessary, especially in the range of low carbon steels, in order to obtain the specified C-content. The specified C-content can be achieved at higher rates of decarburisation, provided the furnace can withstand high (Σ Fe), relatively acid slag and high temperatures.

Low-carbon steels (0.01 — 0.03% C) particularly demand a lower refining rate even in a hot running furnace with highly oxidised slag. For manufacturing such steels, it may be necessary to continue the boil deliberately until a very high temperature is reached. This can be achieved by recarburising the bath several times and prolonging the boil³. Another suitable method should be the blowing of oxygen through water-cooled lance into the bath

which would not only raise the temperature rapidly (by the exothermic heat of oxidation of iron) but also facilitate decarburisation by supplying a large volume of bubbles. The facility of bubble formation and, therefore, an extensive decarburisation (by maintaining the slag highly oxidised with ore additions) is possible in shallow hearths (smaller ferro-static pressure) rather than in deeper ones.

(e) A study of the Figs. 5.4 and 5.5 brings out the effect of higher temperatures on the carbon reaction. An increase in temperature decreases the iron demand of the slag, increases the decarburisation rate and leads to lower C-content. Since the slag composition remains more or less unchanged during the refining period, it is best to study the influence of increasing temperature on the carbon elimination of basic open-hearth metal under a slag of constant composition. Fig. 5.6 has been constructed on the assumption of a bath having initial C-content of 1% under a slag of composition :

$$\begin{aligned}(\Sigma \text{Fe}) &= 10\%; (\Sigma \text{CaO})' = 40\%; (\Sigma \text{SiO}_2) = 20\%; \\(\Sigma \text{MnO}) &= 10\%.\end{aligned}$$

The curves in the figure show a horizontal approach, after an initial declination, which denotes the end of decarburisation or $V=0$. The final or equilibrium carbon content is lower, the higher the temperature. Since higher the temperature, the greater is the oxidation potential of the slag and bath, it is evident that a hotter furnace will be 'off the boil' at lower C-content with a higher decarburisation rate than a colder one.

The importance of proper heating facilities, especially in modern high capacity furnaces, is very apparent. In furnaces with inadequate heating arrangements, the decarburisation can be increased mainly by raising the oxidation potential of slag and bath by reducing the lime/silica ratio and adding iron ore. Reducing the basicity will certainly affect desulphurisation and dephosphorisation (which require high lime), while large ore additions have certain cooling effect which lowers the decarburisation rate itself. (The loss of heat due to ore addition is given on p. 205).

The only course remaining in a badly working furnace is, instead of too much oreing, to recarburise the bath and continue decar-

burisation which improves the heat transfer due to the turbulence caused by further 'boil'.

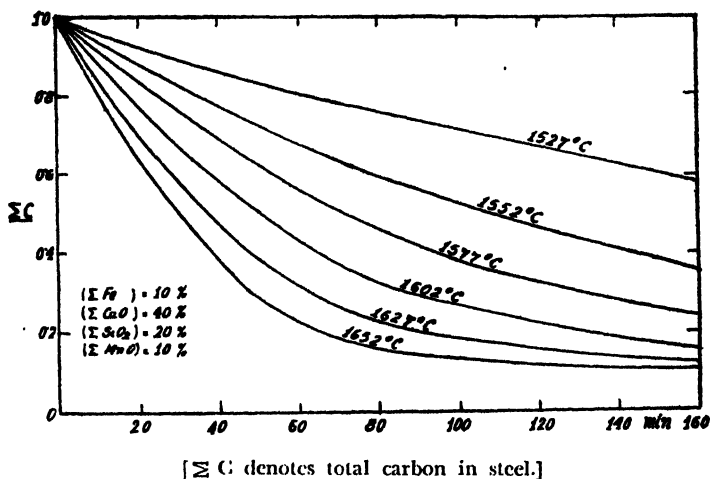


Fig. 5.6—Variation of carbon elimination with time in basic open-hearth at different temperatures under a slag of constant composition. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

In furnaces where rapid heating is possible, the velocity of decarburisation may be too fast which may have a deleterious effect on the steel quality (removal of dissolved gases being inadequate; also at high T the heating rate may not keep pace with the simultaneous increase of m.p.). In such cases, the decarburisation may be suppressed by lowering the (FeO) -activity in the slag, which may be effected through increasing the lime or lowering the total iron content or both. It follows that, in a hot furnace, the bath is less oxidised than in a cold one, provided the slag composition and decarburisation rate are the same. This may also be the reason why, specially the German melters, put so much importance on 'manganese reversion' as, to say, the barometer of adequate steel temperature and quality. A hot bath, since it is less oxidised, facilitates the reduction of manganese from slag which is further boosted by the endothermic reaction $Fe + MnO \rightarrow Mn + FeO$; the reaction proceeds to the right with increasing temperature.

It is desired to impress here the profound importance of decarburisation on the steel quality. The oxygen at the end of

refining should be as low as possible so that minimum quantity of non-metallic inclusions may be formed when the oxygen is removed by deoxidisers. The minimum oxygen is approached as the C-O reaction nears equilibrium. At the beginning of refining, the slag is rich in iron oxide and contains relatively small amounts of lime. The oxidising power of this slag will change, as the refining progresses, depending upon the change in basicity, the velocity of decarburisation and the rate of diffusion of oxygen from the flame through the slag. Effecting a decrease in the oxidising power of the slag by increasing the basicity is limited by the difficulty of dissolving lime, especially with low iron slags. Since flame oxidation is fairly constant, the only other way to decrease the oxidising power is ample, active and speedy decarburisation which would bring the (FeO)-slag, as far as possible, to the level nearing equilibrium with bath carbon. (We have seen on p. 187 that the oxygen potential of slag is consistently higher than that of the bath, except at very low C-contents.) The oxygen in bath, in such a case, would be approximating that in equilibrium with the carbon desired. The inclusions formed by deoxidation would, therefore, be minimum. The reduction in the oxygen potential of the slag would necessarily induce reduction of manganese to the bath and hence the importance of Mn-reversion (*cf.* p. 235).

The necessity of a profuse and active decarburisation is, therefore, apparent for at least a partial reduction of oxygen in slag and metal, apart from the beneficial effect of 'washing away' of the gases and inclusions (*cf.* pp. 380-382). This can, however, be achieved only by a proper slag control. In this context, we may realise the importance of Schenck's recommendation³⁰ of refining with a slag of basicity ~ 2.7 . From Fig. 4.5, this basicity imparts highest (FeO)-activity to the slag which may effect the desired vigour of the 'boil'.

*Use of Oxygen*³¹

In the basic open-hearth operation, the oxidation of carbon at low C-level proceeds at a slow rate. As the C-level drops, the equilibrium oxygen value increases simultaneously because $[C] \cdot [O] = 0.0025$. Since the bath needs or should have an extra-oxygen $\Delta[O]$ for affording the necessary driving force, it is clear that an increasingly greater amount of oxygen has to be supplied

to the bath as the C-level falls, a part of which must necessarily be incorporated in the slag. Fig. 5.7⁸¹ shows that the oxygen-dissolved in metal and the oxygen-content of slag, (FeO), rise as % [C] is lowered under average open-hearth conditions. The [O] values are actual and do not correspond to the equilibrium values for the given [C] contents. From the figure, as C decreases, an increasing amount of oxygen goes to slag and bath. The increased requirement of oxygen can be fed by ore, the rate of feeding being however, limited by the rate of firing the furnace. The reaction of ore and carbon is endothermic and a bath at 1,600°C fed with 1 lb. of ore/min./t (3 cu.ft. oxygen) would cool down at a rate of 2.5°F/min.⁸¹ Thus, with heavy ore feed and without simultaneous adequate heating of the bath, the metal may freeze. The rate of feeding becomes dependent upon the heating rate and at low C-contents, when increasing amount of oxygen is necessary, a high rate of feeding can only be realised if sufficient heat is put in the bath to counteract the decrease in bath temperature.

When the rate of firing or the rate of increase of temperature of the bath or the heat input is constant, the corresponding

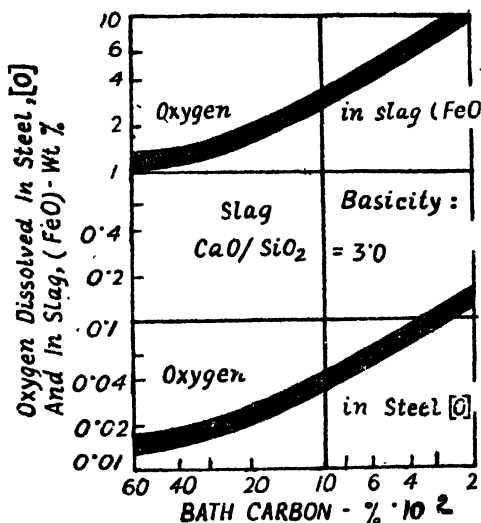


Fig. 5.7—Progress of oxygen dissolved in bath and oxygen content (FeO) of slag with decarburisation under average basic openhearth conditions. (By courtesy of Iron & Steel Engineer).

rate of ore-feeding, which must also be maintained at a commensurate rate, is also constant, i.e. oxygen input is also constant. At constant oxygen-input, as carbon falls, there is a rapid decrease

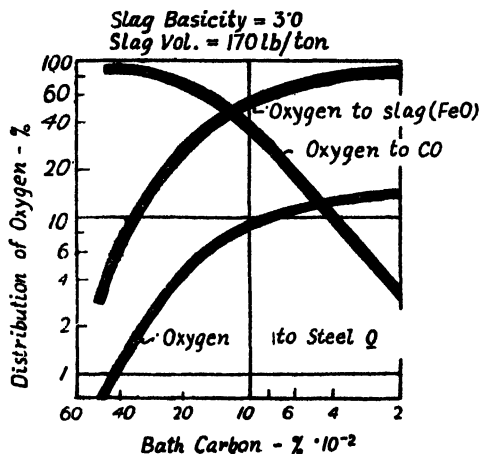


Fig. 5.8—Theoretical relationship between distribution of total oxygen in basic openhearth bath and carbon content during normal decarburisation. (By courtesy of Iron & Steel Engineer).

of oxygen available for decarburisation. Thus, the rate of decarburisation decreases with decreasing C-content. This is borne out from Fig. 5.8 which shows the theoretical distribution of total oxygen in the open-hearth during normal decarburisation at various C-contents. As for example, at 0.5% C, about 95% of available oxygen reacts with carbon and 5% is absorbed by the metal and slag; while, at 0.05% C, about 85% is absorbed by the metal and slag and only 15% reacts with carbon. These values are, of course, dependent on the basicity and the amount of slag which in this case are $\text{CaO/SiO}_2=3$ and 170 lbs./ton respectively.

The situation changes if, instead of as ore, the oxygen is supplied in gaseous form. At 0.1% C, gaseous oxygen at the rate of 3 cu.ft/min./ton at 1,600°C would increase the bath temperature at a rate of 3.5°F/min. Thus, the rate of feeding oxygen gas can be increased to any amount, limited only by the splashing of the bath and fuming of FeO consequent upon high rate of injection. There is no danger of any metal freeze-up even

at very high rates of decarburisation. The advantage of ore feed, however, is that it increases the yield of metallics, iron ore supplying the iron. With one or two water-cooled lances or jets, oxygen flow of 80,000 cu.ft./hour presents no difficulty. An equivalent amount of oxygen in the form of ore (25,000 lbs. of ore) at the same rate of feed would simply freeze up the metal.

Since after the Second World War, in order to raise steel production as well as to compete with the new and rapidly developing oxygen-lancing converter processes, the gaseous oxygen is being increasingly used in open-hearth for obtaining high rates of carbon removal with simultaneous delivery of high temperature heat to the bath. Taking into consideration the fact that each minute of furnace time gained means a saving of about £1/- 'cost above', it is clear from Fig. 5.9³¹ why oxygen injection is economical and that too at low-C rather than at high C-contents. The figure shows the curves of actual rate of decarburisation using oxygen and ore

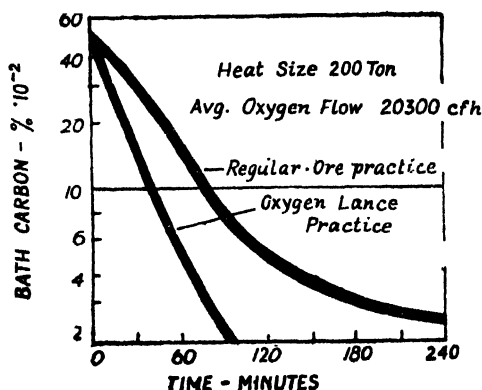


Fig. 5.9—Different rates of decarburisation in openhearth during regular ore and oxygen lance practices. (By courtesy of Iron & Steel Engineer).

for a 200-ton heat. For example, carbon removal from 0.2 to 0.08% (a drop of 0.12%) takes 22 min. for oxygen and 40 min. for ore, the saving in time being 18 min. Now, for the same drop but from 0.15 to 0.03% [C], it takes 47 min. and 115 min. for oxygen and ore respectively, the time saved being 68 min.

Oxygen must be used judiciously. If the furnace is working hot, advantage should be taken of, to use ore for C-oxidation. This

will mean increased yield of metal by using inexpensive ore. Since all reactions of ore with slag and metal are endothermic while those with oxygen are exothermic, the latter can be used profitably when the furnace is cold and inactive and needs heat. The overall production rate in open-hearth depends primarily upon the availability of oxygen for chemical reaction with carbon as well as that of high temperature heat in excess of bath temperature. When and how much of oxygen should replace the ore would depend entirely upon the run of the heat.

The importance of slag bulk must not, however, be overlooked. From Fig. 5.8, large amounts of iron and oxygen go to the slag as FeO, at [C]-contents below 0.1%. Therefore, when using oxygen, the slag bulk should be kept to the minimum, even by a second-flush off which may be unnecessary otherwise.

Acid Open-hearth³

The relations between carbon reaction, temperature and free (FeO) described under basic open-hearth are applicable to acid hearth as well. Since acid slags consist mainly of FeO-MnO-SiO₂, it is only necessary to find the slag compositions for various free-(FeO)-contents. In the same way as in Fig. 5.4, the [C]-contents have been plotted in Fig. 5.10³ as functions of total (Σ FeO) and (Σ MnO) contents (the rest being silica) at which $v=0$, i.e. at equilibrium, when the bath is quiet. The minimum attainable carbon-contents under various slag compositions are evident from the figure. It is possible to attain a certain [C]-content at lower (Σ FeO) if the temperatures are higher and more of silica is replaced by MnO. If FeO and MnO in the slag or the temperature are increased, lower [C]-contents can be reached. The same conditions apply to the rate of decarburisation as well; thus, an increase in temperature or (FeO) or (MnO), would increase it. This is clear in Fig. 5.11 which is valid for 1,527°C only. It may be noted that addition of iron ore is more efficacious than manganese ore in speeding up the boil.

The speed and extent of carbon elimination with increasing temperature, for constant slag composition, is similar to Fig. 5.6 in sense. An acid open-hearth furnace, with adequate heating facilities, would need a smaller refining time than a colder one, provided

the slag composition is same and similar rate of decarburisation is followed.

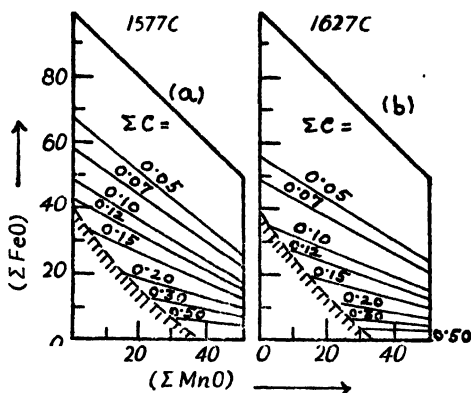


Fig. 5.10—Composition of acid openhearth slag over steel bath of various carbon contents when boiling has ceased. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

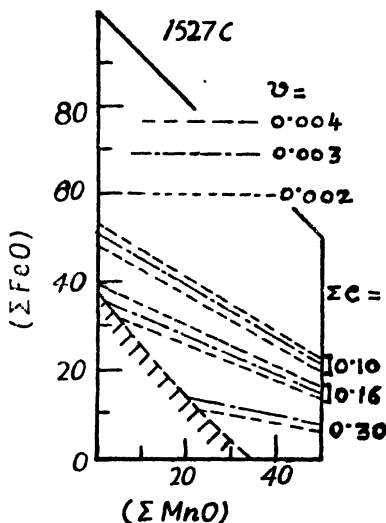


Fig. 5.11—Composition of acid openhearth slag over steel bath with C-contents traversed with different rates of decarburisation at 1527°C. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

Since FeO is strongly corrosive to the acid silica lining, it is imperative that the slag contains iron oxide as low as possible.

That is why the manufacture of low-carbon steels in acid process should be avoided because a decarburisation to the extent of only 0.1 — 0.15% C requires a considerable amount of (\approx FeO) in slag. The question, whether the highly corrosive high-FeO fluid slag would attack the hearth bottom (because they are not directly in contact with each other), is irrelevant since they have to be in equilibrium with each other if slag/metal and metal/hearth are in equilibrium.

An important question arises from the fact that, in the acid furnaces, the carbon reaction cannot be considered alone but together with that of Si and Mn which are invariably present in the bath. The equilibrium relations between these three elements under laboratory conditions have been elaborately discussed on p. 92. Their reactions in acid open-hearth practice will be discussed on p. 248. It may suffice here to say that the carbon elimination depends greatly upon bubble formation and the reaction between [C] and [O] takes place at the hearth bottom where small pores and crevices facilitate the nucleation of CO-bubbles. The initial slag with high iron-oxide is slowly replaced by high silica and manganese oxide slags, whose viscosity increases as (FeO) becomes less and less. The oxygen transfer to the bath is much reduced, as the slag becomes viscous, which induces carbon to react with the hearth and reduce silica to silicon. It is fallacious to think that acid steels are more clean because of the deoxidising action of the reduced silicon. It is rather because of the presence of low oxygen (due to sluggish transfer from slag) in the bath, which induces reduction of silicon to the metal by carbon.

The rate and extent of decarburisation can be controlled at will in acid open-hearth by increasing or cutting-back the fuel. Further, the oxygen supply to metal from slag is performed not by FeO only but MnO also plays a part, depending upon the relative amounts of each in the slag. This has already been discussed on pp. 51 and 177.

Acid Bessemer

The relation between carbon and oxygen is shown in Fig. 5.12. The rate of carbon removal depends upon the rate of oxygen delivery. It is doubtful whether the oxygen potential of slag plays

any definite role. The reader may also refer to discussions on pp. 25 and 348.

Thomas process

In the Thomas Process, carbon is eliminated at a very fast rate, about 0.25% C/min, and phosphorus removal is largely held up until a carbon concentration of $\sim 0.02\%$ in the metal is reached. The aerial oxygen oxidises iron into FeO. It reacts with C to form CO gas which can evolve when its pressure is higher than the sum of the atmospheric and hydrostatic pressures of metal and slag. The evolution of CO is facilitated in the presence of nitrogen bubbles and in those parts, where the facility of nucleation is absent, there is a build-up of oxygen similar to what happens in the open-hearth. Although, because of the numerous nitrogen bubbles acting as nuclei for CO evolution, the C-O reaction should reach equilibrium, infact, however, the oxygen-content lies much higher than given by the equilibrium relations (*cf.* Fig. 5.12). Only below $\sim 0.05\%$ [C], the equilibrium value is reached and even lower value attained.

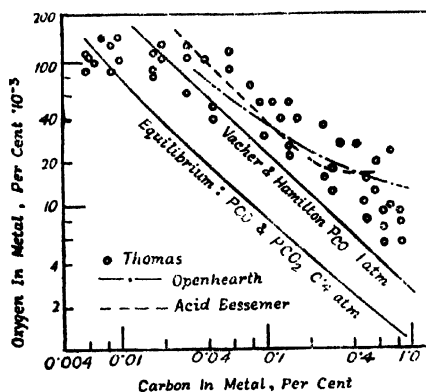


Fig. 5.12—Relation between carbon & oxygen contents of steel in different processes and under equilibrium conditions.

Carbon is an extremely good reducing agent as long as facilities for CO-evolution are present. During the Thomas blow, the oxygen level in metal remains below 0.012% so long sufficient carbon is present and the value is only exceeded when carbon

falls below $\sim 0.2\%$. The ultimate carbon content reached is about $0.02 - 0.03\%$ and very seldom a value of 0.01 is attained. Surprisingly, however, CO ($\sim 1\%$) is found in the escaping gases even when the carbon removal is complete. It has been assumed that the converter lining and bottom, which still contain coked tar, supply the carbon. Theoretically, however it is possible to reach a carbon content of less than 0.01% as shown below³² :

From the Fe-C-O equilibrium system (*cf.* p. 67), pure oxygen reacts with an Fe-C alloy with the formation of CO and CO₂ in the ratio of 6 : 1 (i.e. 86 and 14%). In presence of pure oxygen or pure FeO, the maximum oxygen solubility is 0.23% at $1,600^\circ\text{C}$. Neglecting CO₂, the minimum $[C] = 0.0025/0.23 = 0.0108$. At 14% CO₂, i.e. $p_{\text{CO}} = 0.86$, $[C]$ (minimum) $= 0.0085\%$. In the case of blowing of air or oxygen-enriched air, the conditions are different since CO is diluted with nitrogen. For air, 21 vol % of oxygen burns to give 42 vol % CO and 79 vol % N₂. Therefore, $p_{\text{CO}} = 42/121 = 0.35$ & $[C]$ (minimum) $= 0.0025 \cdot 0.35 / 0.23 = 0.0035\%$. If it is assumed that, at the start of dephosphorisation the oxygen content $= 0.04\%$ (*cf.* p. 271), then $[C] = 0.0025 \cdot 0.35 / 0.04 = 0.021\%$ at the transition. This has been found to be really the case in Thomas process when the carbon elimination ends and dephosphorisation starts. During the dephosphorisation, the oxygen at the disposal of carbon is very small. Pottgiesser³² has calculated that the theoretically attainable $[C]$ for air-blow is $0.03 \cdot 10^{-37}\%$ and $0.01 \cdot 10^{-18}\%$ for oxygen-enriched air (35 % O₂). This signifies that even at low $[C]$, attained in the converter, it still possesses a great reducing action on oxygen where air enters the metal.

Since carbon is oxidised only by the metal oxygen, it is desirable to see how both behave during the Thomas process. After the elimination of Si and Mn (during which period some carbon is also oxidised), carbon is the only element (except iron which is oxidised and a part simultaneously reduced by C) which undergoes reaction before the phosphorus removal starts. Fig. 8.3 shows the behaviour of $[C]$ and $[O]$. Instead of drawing them against the blow-time as is usual, they are related to oxygen consumed in Nm³ which is after all the real variable. Again, in the figure, the 'transition' is defined not as the end of decarburisation as is normally depicted but, rather, as the beginning of dephosphorisation indi-

cated by a sharp increase in bath temperature.³² Thus the 'transition', here, takes place at $\sim 0.10\%$ [C] and not at 0.02% [C] and the dephosphorisation starts, according to this definition, before the carbon has been completely eliminated. It can be seen from the figure that the oxygen in metal increases even before the transition and continues to do so after the transition and the end of the carbon reaction coincides with the apex of the oxygen-hump. The metal oxygen reacts with carbon even during the dephosphorisation. During the period of increasing oxygen, the carbon-content decreases and a small amount of CO is always detectable. Only when the oxygen requirement of phosphorus is enormous and the oxygen-content suddenly falls, does the carbon monoxide evolved become negligible.

The low carbon-content reached in this process no longer possesses any influence on metal oxygen in practice. The iron oxide activity of the slag takes the upper hand and determines the end-oxygen contents of metal. This is borne out in Fig. 5.12 where oxygen lies below the equilibrium curve at low C-contents. The equilibrium line has been calculated for a total $\text{CO} + \text{CO}_2$ pressure of 0.4 atm, taking into consideration the rise of metal temperature during the blow as well as the CO_2 per cent in the outgoing gas.³³ At higher C-contents, the oxygen values are much higher than the equilibrium values at $p_{\text{CO}} + p_{\text{CO}_2} = 0.4$ atm. The distance gradually decreases with carbon and at $\sim 0.01\%$ [C] the equilibrium curve is reached and then subsequently crossed to lower values at lower [C]. For comparison, the Vacher-Hamilton's equilibrium curve, air-blown acid Bessemer curve as well as the average oxygen values in open-hearth are also shown.

Oxygen-enriched air process

Since the input of oxygen is more in this case than in the air-blown process, it is natural that the carbon removal is faster. But this rate is slower *vis-à-vis* dephosphorisation rate as compared to their rates in normal air-process. This means that for the same end-[P] content, the oxygen-enriched process leads to more end-[C] content than in the aerial process. This is probably because the smaller amounts of nitrogen in the oxygen-enriched process leave less numerous nitrogen-bubbles to act as

nuclei for CO-evolution and, therefore, the rate of carbon removal is slower; the weaker deoxidising action of carbon enables high oxygen-build up in the metal which maintains the normal rate of dephosphorisation. This is evident³² from Fig. 8.5 where $[C]$ is higher than in the normal process, for the same $[P]$. In the C-O equilibrium diagram, $[O]$ lies much below³² the equilibrium for $p_{CO} = 1$ atm (Fig. 5.14).

Fig. 5.13 shows the relation between $[C]$ and the Mn-content of metal and (Fe)-content of the slag. Although the spread of the results of Pottgiesser is wide, yet a relation between $[C]$ and (Fe)- on the one hand, and $[C]$ and $[Mn]$ on the other does exist. Both these functions—(Fe) and Mn—are, however, measures of the extent of slag oxidation.

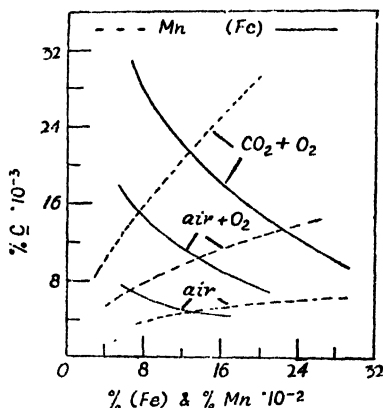


Fig. 5.13—Relations between carbon & manganese in steel and Iron in slag in Thomas process blown with air, oxygen-enriched air, & oxygen-carbon dioxide mixture. (H. Pottgiesser, Jr., *Stahl und Eisen*, 78, 1958, 291-98).

Oxygen-carbon dioxide process

The behaviour of carbon in O_2 - CO_2 process is shown in Fig. 5.14. Thomas iron blown with O_2 - CO_2 mixture shows that $[C]$ and $[O]$ contents are in the neighbourhood of the Vacher-Hamilton's line, in contrast to the normal and oxygen-enriched processes. Oxygen, however, lies below the equilibrium curve. This may be because the deoxidising action of $[P]$ lowers the $[O]$ -content.

Fig. 5.13 shows the relation of $[C]$ with Mn and (Fe). The end- $[C]$ content of the melt is higher in this process and the figure

shows that (Fe) is much lower and Mn higher than the other two processes. Fig. 8.5 shows the relation between [P] and [C] before and after the dephosphorisation.³² The dephosphorisation in this process starts a little earlier and ends at a higher [C]

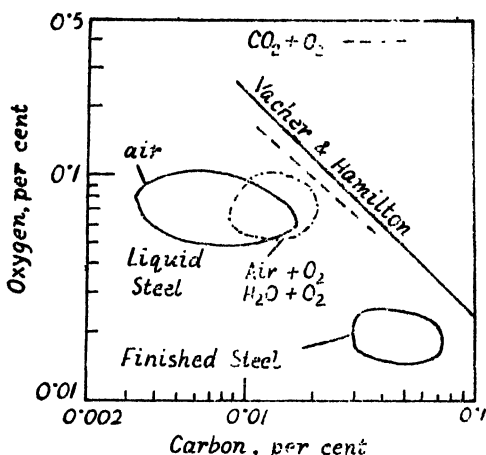


Fig. 5.14—Relation between the carbon and oxygen-contents of liquid steel in the normal as well as modified oxygen-enriched, oxy-steam and oxy-Carbondioxide Thomas processes. The same relation in the finished steel is shown in the lower right hand corner.

for the same phosphorus than the other two processes. The carbon is no longer so active a deoxidising agent as to deplete the bath of oxygen sufficiently and thus suppress the dephosphorisation or phosphorus oxidation reaction.

Oxygen steelmaking processes

We have seen that the carbon removal from molten steel is greatly dependent upon the facilities of nucleation of bubbles. In the Thomas process the innumerable nitrogen bubbles, acting as nuclei for the formation of CO-bubbles, lead to an almost unhindered decarburisation. In the open-hearth, such a large number of nuclei are not available but the pores and crevices of the hearth, unwetted by steel, are the sources of such nuclei. However, once the boil starts and continues throughout the bath, the rate of carbon reaction becomes dependent on the rate of diffusion of oxygen from the slag to the metal, or rather to the place where carbon reacts with oxygen with the evolution of CO. The dis-

tance of carbon and oxygen from their equilibrium values determines the diffusion velocity. The transport of oxygen can be accelerated by increasing the distance of equilibrium between the slag and the bath. In the stationary top-blown converters, the direct impingement of oxygen oxidises the slag greatly in a short time, which increases the oxygen delivery (when the boil starts) to the bath more rapidly than in the open-hearth. In both the cases there is an absence of inter-mixing of slag and metal. There is no direct reaction between the slag and the metal except at their interface at the top. The importance of diffusion becomes less in the rotating converters and with the increasing speed of rotation the direct reaction between the slag and the metal, due to intermixing throughout the bath, assumes importance and becomes the rate controlling factor. With stationary or slowly rotating converters, reactions take place more or less at the slag/metal boundary and the reaction velocity exceeds the speed of transport of the reacting molecules to the zone of reaction. With high rotating speeds, the reacting surface increases enormously due to intermixing between slag and metal, and from a mere interfacial reaction we rather get a reaction that occurs throughout the mass of the metal and the slag. Thus the velocity of decarburisation can be much more accelerated in the rotating converters than in the stationary ones, and much more so in the elliptical than in the cylindrical types. In cylindrical converters the intermixing is very small, only a little more than in the open-hearth or LD. It must, however, be borne in mind that if the speed of rotation is very high so that the intermixing and decarburisation are of the order as in the Thomas process, then the phosphorus removal will be delayed till the completion of decarburisation. Carbon is an inferior reducing agent as long as CO-evolution is suppressed and, therefore, allows the oxidation potential of metal to rise high enough to effect dephosphorisation. As we will see later, a bath oxygen of 0.03-0.04% is necessary for phosphorus reaction to take place (of course, if a liquid base is present to form stable phosphate). An unhindered carbon reaction will not allow such a high build up of oxygen in the bath until a value as low as 0.1% C is reached.

In this section, the mechanism of carbon reaction in rotating elliptical and cylindrical converters is considered, since this dis-

cussion will clarify the mechanism of decarburisation, not only in all the oxygen steelmaking processes, but also in the open-hearth and electric furnaces. The elliptical converter is still in an experimental stage but the report on the pilot plant project by Hardt *et al.*³⁴ makes the mechanism of carbon removal simple to understand.

Rotating Converters

Elliptical vessel : The speed of carbon removal depends upon the speed of rotation and amount of oxygen supplied in unit time. For a given rate of oxygen injection, the decarburisation increases with increase of rotation, more so in the elliptical than in the cylindrical vessels. This is because of thorough intermixing between the slag and the metal in the former, which is more or less absent in the latter type of vessel. Fig. 5.15a shows the relation between the velocity of decarburisation and the number of rotations per min in an elliptical vessel. As rotation increases, the nucleation of bubbles is facilitated and the oxygen transport is accelerated due to turbulence. Both these factors favour carbon reaction. Therefore, the decarburisation can be controlled at will by varying the rotation rate, the highest speed of decarburisation being limited by the oxygen activity of slag and amount of oxygen supplied. For a vessel with a given dimension, there is an optimum

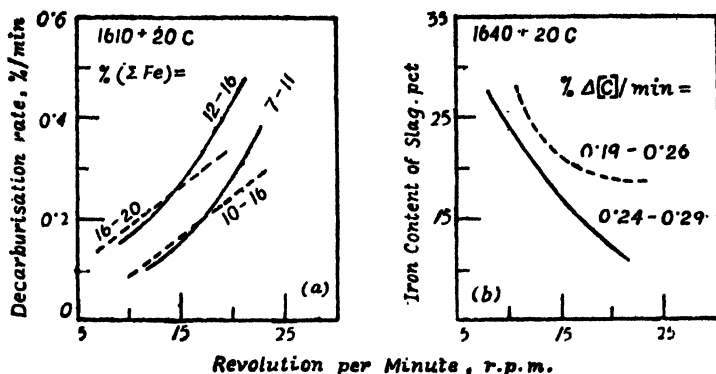


Fig. 5.15—Relation between speed of rotation and (a) decarburisation rate under slag with different iron contents and (b) iron content of slag with different rates of decarburisation. Initial C-content not shown. Solid lines, elliptical vessel; broken lines, cylindrical vessel. (P. E. Hardt, G. Vocke & H. Schenck, *Stahl und Eisen*, 81, 1961, 311-20).

oxygen supply and rotation speed beyond which the carbon removal will be so rapid as to precede dephosphorisation or even effect a rephosphorisation.

Fig. 5.15a also shows that the decarburisation velocity depends upon (Fe)-slag and for a given rotation rate, the velocity is higher at higher (Fe)-contents. This is not contradictory to the nucleation mechanism of carbon reaction. If the number of rotations is kept constant, the extent of nucleation will also be the same for high or low (Fe). Therefore, once the carbon reaction starts, the oxygen transport through the metal should determine the decarburisation velocity. Thus, a higher (Fe) or for that matter, higher supply rate of oxygen should increase the carbon removal. Further, there is an intimate relation between (Fe) and the rotation, for a given velocity of decarburisation, as shown in Fig. 5.15b. According to the figure, a high (Fe) with low rotation leads to no better decarburisation as by low (Fe) and high rotation. The reason being inspite of the high (FeO)-activity in a slowly rotating vessel, because of inadequate inter-mixing, no more oxygen enters the bath than in the case of a low (FeO)-activity slag with high rotating speed. As for example, a speed of 9 r.p.m. needs 25% (Fe) and a speed of 20 r.p.m. only 11.5% (Fe) for attaining the same velocity of decarburisation.

Apart from the influence of speed of rotation, temperature and iron-content of slag, the initial content of carbon has a decisive influence on the decarburisation velocity. The velocity decreases with decreasing initial [C]-content under otherwise same conditions. This also happens in the open-hearth. In order to compensate the falling rate of carbon removal, the speed of rotation has to increase correspondingly. This flexibility of controlling the decarburisation is totally absent in the open-hearth. There, the decarburisation can only be increased at the cost of high iron-content in slag.

Cylindrical vessel : The decarburisation in cylindrical vessels follows the same pattern as in elliptical ones, the difference being in the rate of the process. The rate rises with increasing rotation but to a lesser extent than in the elliptical vessels. In the latter type, both the facilities of nucleation and intermixing play a part, whereas in the cylindrical vessels the decarburisation increases only because of increased nucleation. The turbulence caused by

CO-evolution facilitates oxygen diffusion. On comparison between the decarburisation curves in Fig. 5.15a, the flatter run of the curves in the cylindrical vessel is at once indicated and, on the other hand, it is clear that higher (Fe) is necessary for the same rates of rotation and decarburisation, than in the case of elliptical vessels. This can only be explained by the slower delivery of oxygen from slag to metal in the cylindrical vessels.

Fig. 5.15a makes it clear that the delivery of oxygen to the bath depends only on the amount of CO evolved. The amount is small because, initially, the [C]-content has been low (0.9-1.5% [C]) and, therefore, the turbulence has also been limited. The flat run of the curve indicates that decarburisation cannot be decisively increased by increasing the r.p.m. This again supports the assumption that once the 'boil' starts, the further rate of decarburisation is determined by the rate of oxygen delivery from slag to bath. In the case of elliptical vessels, the decarburisation rate is low with initially low [C] in bath but the rate rises with increasing r.p.m., since it increases the intermixing and consequently the delivery of oxygen.

As in the elliptical vessels, the (Fe)-slag is related to the r.p.m. (see Fig. 5.15b) in the cylindrical vessels as well. But, for the same rate of decarburisation, the (Fe)-slag is higher in the latter and also, above 17 r.p.m., there is no marked lowering of (Fe). This has significance in the Kaldo process. There, a high (Fe) can be built up with slow rotation in order to favour dephosphorisation (low r.p.m. suppresses the carbon removal as well) and the decarburisation can be increased later by higher r.p.m. with the consequent low end-(Fe) of slag, thus diminishing the iron loss.

With proper control of rotating speed, dephosphorisation can always be made to precede decarburisation in both the types of the vessels. Therefore, the refining time is dependent on the velocity of carbon removal only, which in its turn depends on the rotation speed and rate of oxygen delivery. An increase of both increases decarburisation, the more so in the elliptical vessels. In cylindrical vessels, since the rotation speed has no influence on decarburisation after a certain limiting value, there is an optimum intake of oxygen beyond which free oxygen would escape. In the case of elliptical vessels, this optimum is much higher and

much more oxygen can be consumed with the consequent very large velocity of decarburisation.

The discussions in the foregoing section will help in the understanding of the decarburisation rates in the oxygen-steelmaking processes, the end-oxygen contents in the metal and the iron-content of slag in such processes, as well as how the rate can be influenced by creating a controlled turbulence, so as not to prejudice early dephosphorisation. It may be mentioned again that the dephosphorisation needs high oxygen potentials in the bath and the slag, a liquid reactive basic slag and sufficient turbulence for increasing the slag/metal interface. Carbon is a strong reducing agent in the presence of facilities for nucleation and, therefore, does not allow the oxygen potentials of the metal and slag to rise high enough for dephosphorisation to set in, if the carbon-oxygen reaction proceeds unhindered. Top-blowing of oxygen in stationary and rotating converters, with controlled r.p.m., helps to suppress the carbon reaction and permits sufficient build-up of oxygen at the slag/metal interface, as in the open-hearth (where carbon reaction occurs at the hearth bottom), so as to effect an early removal of phosphorus.

L D Process : This process is metallurgically similar to the open-hearth. The carbon reaction will be evident from the discussions on pp. 216, 274-78 and from Figs. 8.14, 2.6 and 10.4.

Kaldo and Rotor processes : The principles involved in the carbon reaction have been discussed in the preceding sections. They will further be evident from Figs. 10.4, 2.8 and 2.10 and discussions on pp. 33-38, 217-19 and 274-78.

Electric Steel : The carbon reaction is similar to that in the open-hearths. The reader may also refer to discussions on p. 353.

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THE REACTIONS OF SILICON AND MANGANESE

General

The elements Si and Mn are invariably present in pig iron. The blast furnace metal is the major source of these elements, introduced in the steelmaking furnaces. Their contents depend upon the nature of raw materials employed and the conditions under which iron is made. While Si in iron is unavoidable (although its content can be kept under control in the blast furnace), Mn is generally added deliberately, for without it a reasonably clean steel cannot be made. Manganese also helps to keep the sulphur in pig iron at a low level. In the basic open-hearth, making from low to medium carbon steel, it is usual to have 0.3-0.4% Mn in the metal at melt down to prevent an over-oxidation of the bath.

In basic steelmaking, Si is oxidised more or less completely into silica which is acidic and does not play any significant role in the steel bath, except in so far as that a higher Si-content would require more lime in order to maintain a certain level of basicity. But Mn, which is oxidised to MnO , does not enter the slag entirely and the Mn-content of the metal depends upon the temperature and the composition of the slag. The transfer of Mn from the slag to the metal and *vice versa* is of importance, not only because the metal itself is valuable and, therefore, its loss into the slag by oxidation should be minimised, but also (and it is almost legendary, especially amongst the German steelmakers) its final content in the bath is an indication of the quality of the finished product. It is believed that clean steel is obtained when the metal and slag conditions are such that the transference of Mn from the slag to the metal is favourable. In the acid open-hearth, the reduction of Mn from the slag and of Si from the slag as well as from the silica lining of the hearth play an important part in the process. The extent of the reduction of Si, although not an economic problem, does influence the steel quality.

A knowledge of the oxidation-reduction mechanism of Si and Mn is helpful in ascertaining, qualitatively as well as quantitatively,

the conditions that control or influence the transfer of these elements from the metal to the slag and *vice versa*. If the equilibrium conditions governing the direction of these reactions are known, it would be possible to find, from the constituents present in the metal and the slag, how far the system is away from the equilibrium and how to deal with it, if necessary, to our advantage. The physico-chemical laws which are valid for the oxidation of elements in the converter processes should also be applicable in the open-hearths as well. In the converter, the time taken for the completion of the oxidation reactions is small because of the intimate mixing between the metal, the slag and the air. In the open-hearth, the process lasts considerably longer and, therefore, the conditions for attaining an equilibrium are much more favourable than in the converter. In practice, it has been found that, in the open-hearth, the nearness to the equilibrium of the reactions of the components taking part, viz: Mn, Si, P, S, are considerable.

Steelmaking mostly involves the oxidation of Si, Mn and C. The order of elimination of these elements is as above, although purely from the values of the free-energies of oxidation, the order should be Si, C and Mn. The silicon oxidation has the largest negative value of free-energy and is, therefore, eliminated first during steelmaking. Although, according to free-energy considerations, carbon should be eliminated before manganese, in fact the latter takes the place of second in order because its oxidation is facilitated by its oxidation product MnO going to the slag as silicates and being held there in a state of low activity. Further, the products of oxidation of Si and Mn are solid or liquid slags, whereas that of C is gaseous. The evolution of CO is restricted by the factor of bubble formation or its diffusion into the air bubbles, as in the converters. Both these factors are inherently slow and, therefore, the carbon reaction itself is a much slower process than those of Si and Mn. The effect of temperature is such that the hotter the metal, the slower is the elimination of Si and Mn. In an acid converter, if the metal temperature is high, the silicon reaction is delayed and, before it is completely removed, the carbon reaction starts, thereby causing some silicon to be retained in the bath at the end of the blow (*cf.* Fig. 3.21 and p. 95).

We will discuss at first the reactions of only manganese in the

basic process since silicon is almost completely removed in such a process and is of little significance in the slag-metal reactions. In the acid processes, the reactions of both Si and Mn will be narrated together because their oxidation-reduction follows the same pattern.

Reaction of Manganese in basic processes

The manganese oxidation reaction is exothermic. MnO with its m.p. of $1,750^{\circ}\text{C}$ is almost insoluble in iron. The oxygen in the metal which oxidises Mn, is obtained from (FeO) of the slag. This slag iron oxide always keeps the iron supplied with the necessary oxygen. The reaction may be deemed to take place at the slag-metal interface, according to Eq. 3.15. The manganese equilibrium reaction under pure FeO-MnO slag and the equilibrium constants are given by Eqs. 3.15-3.17. The constants have been calculated by using mol fraction or wt. % of (FeO) and (MnO). The constant K_{Mn} has been found to decrease and the [Mn] to increase, with the increase in temperature. In complex slags, the constant is no longer non-variable and varies according to the basicity or the acidity of the slag, since the activities of FeO and MnO also undergo changes. (In terms of activities the constant must, however, be invariable.) The reversible reaction in the basic process is different from that in the acid. In the basic slag, the MnO exists more or less as a 'free oxide', whereas in the acid slag, which is saturated with silica, the MnO is bound as a silicate. The reduction of Mn in the basic process is, thus, much easier than in the acid one.

Tammann and Oelsen¹ have calculated K_{Mn} from various steelmaking data and shown the tremendous influence of the slag basicity on the constant. According to them, the constant decreases with increasing basicity. They conclude that the K_{Mn} behaves as a constant when $(\sum \text{CaO} - 1.18 \sum \text{P}_2\text{O}_5)$ is more than the lime necessary to form $2\text{CaO} \cdot \text{SiO}_2$ and is independent of lime further. But if it is smaller, then the K_{Mn} increases with decreasing lime, i.e. the oxidation of Mn is facilitated. Maurer and Bischof² have studied the influence of acidity and basicity of the slags on K_{Mn} . They have observed that P_2O_5 increases the K_{Mn} , which is probably because of an effective decrease of lime due to the formation of calcium phosphate. MgO increases the

K_{Mn} , probably because it loses its basicity at high temperatures. Alumina decreases the constant with low- and increases it with high-slag silica contents. They explain the phenomenon by assuming the formation of $FeO-Al_2O_3$ at low silica (which probably decreases the a_{FeO}) and Al-Mn-silicate at high silica contents (which probably decreases the a_{MnO}). Further observations show that Si and P shift the equilibrium positions of manganese (this is probably because of a change in the activity of [Mn] in the presence of Si and P, the formations of a silicide and a phosphide being anticipated). The variation of the K_{Mn} with the temperature has been found to be a function of, especially, SiO_2 content.

Other investigators^{3,4} have also arrived at almost the same conclusions in their works on the manganese equilibria. They have all used weight per cent in the equilibrium equation.

In view of the failure of the earlier attempts to evolve a 'true' constant for the manganese equilibrium, Schenck and Riess⁵ have made an attempt to find it, basing their calculations on the 'free oxide' theory. For every slag, at a given temperature, there are present (FeO) and (MnO) as free oxides, for the given concentrations of (ΣFe), (ΣMn), (ΣSiO_2), (ΣCaO), (ΣP_2O_5), as obtained by analysis. These 'free' values could be obtained from the charts they have produced from various steelmaking data.⁶ They have found that the manganese reaction leads to an equilibrium between the 'free' (FeO) and (MnO) concentrations in the slag and [Mn] in the metal governed by Körber and Oelson's K'_{Mn} value⁷ under pure FeO-MnO slag.

$$\log K'_{Mn} = \log (FeO) \cdot [Mn] / (MnO) = - 6,232/T + 3.026$$

6.1

These workers⁵ have found that the [Mn]-content, in the absence of more than 0.02% [P] in the metal and 6% (MgO) in the slag, increases with (i) increase in the temperature, (ii) increase in the (ΣMnO) of the slag (iii) increase in the (CaO') of the slag where (CaO') = (ΣCaO) - 1.57 (ΣP_2O_5) (iv) decrease in the (ΣFe) of the slag, (v) decrease in the (ΣSiO_2) of the slag. An increase in the [P]-content increases the [Mn], whereas an increase in the (MgO) decreases it. They have

drawn diagrams which show the influence of temperature, ΣFeO), (ΣMnO), (ΣCaO), etc. on K'_{Mn} .

We have already discussed the practical utility but the theoretical unsoundness of Schenck's free oxide theory. A more radical approach should be the use of the activities instead of the concentrations for finding the constant of the manganese reaction (Eq. 3.15) :

$$\log K_{\text{Mn}} = \log a_{\text{MnO}} / (a_{\text{FeO}} \cdot \% [\text{Mn}]) = 7,406/T - 3.436 \quad 6.2$$

Eq. 6.2⁸ can be successfully used for calculating the [Mn] under a given slag at a known temperature from the activities of (FeO) and (MnO) as given in Figs. 4.4 and 4.7. This equation further helps us to find whether the Mn-reaction reaches equilibrium in practical steelmaking, by comparing the calculated and analytical values of [Mn]. It further enables the operator of melting shops to adjust the slag composition and the temperature for obtaining the desired manganese in steel.

Example⁸ : Determination of [Mn] in equilibrium with a known slag.

Let the compositions of the slag and the mol fractions of the components be as given on p. 151, Table 4.1. Since $N_{\text{FeO}} = 0.07$, Fig. 4.7 (a) and (b) are to be used. From (a), $a_{\text{MnO}} = 0.18$ and from (b), $a_{\text{MnO}} = 0.13$, when $N_{\text{CaO}+\text{MgO}} = 0.58$ and $N_{\text{MnO}} = 0.06$. Linear interpolation, between these two values, gives $a_{\text{MnO}} = 0.16$ at $N_{\text{FeO}} = 0.07$. From Fig. 4.4(a) $a_{\text{FeO}} = 0.34$ for the given slag. At, say, 1627°C , $K_{\text{Mn}} = 2.897$ from Eq. 6.2 and, therefore,

$$[\text{Mn}] = 0.16 / (0.34 \cdot 2.897) = 0.163\%.$$

Basic Open-hearth

The behaviour of Mn in the basic open-hearth is of importance not only for the economy of the element but also for following the overall course of the process. In order to find how Mn in the metal changes with the change in the temperature and slag compositions, we must, at first, know the equilibrium concentration of [Mn] for a given slag at a given temperature. The movement of Mn from the metal to the slag or from the slag to the metal can be best studied from the distance of [Mn] from the

equilibrium values. Thus, the primary aim for any study of the manganese partition should be to ascertain whether an equilibrium between the slag and the metal, with regard to the manganese reaction, is at all reached during the course of any particular steelmaking process. If the equilibrium is reached, it would not be difficult to find, during the heats, the distance of the actual $[Mn]$ from the equilibrium concentration. From the known value of K_{Mn} at any temperature, the melter is in a position to adjust the slag compositions in order to attain the necessary activities of MnO and FeO , so that a maximum manganese recovery is possible. The variation of the slag composition can, however, be done only within limits, taking care of the $[P]$ and $[S]$ contents of the metal.

There is no dispute regarding the fact that the manganese reaction reaches equilibrium in the basic open-hearth practice. A comparison between the analysed and the calculated values of $[Mn]$ with the help of Eq. 6.2 and the activities of MnO and FeO for different slag compositions (*cf.* p. 226), shows that an equilibrium is reached between the slag and the metal for all practical purposes.⁸ The equality of the observed and the calculated values of $[Mn]$ shows that the manganese distribution between the slag and the metal, in both the acid and the basic open-hearth furnaces, is also independent of the metal carbon. Further, this equilibrium has been found to be quickly re-established after being disturbed by changes in the temperatures and/or additions of pig iron, lime, iron and manganese ores, ferro-manganese, etc., which indicates that the transfer of manganese between the metal and the slag is a rapid process.

Larsen⁹ and Schenck and Riess^{5,6} have also shown that an equilibrium is reached, especially at the end of the heat, after additions of Mn-ore and ferro-manganese. In the case of Mn-ore addition, the (MnO) -slag increases, which gradually induces both its reduction as well as the transfer of Mn to the bath till the equilibrium is attained. On the other hand, the addition of Fe-Mn to the bath causes a sudden increase of $[Mn]$ to a peak value which subsequently decreases, due to oxidation, until the equilibrium value is reached. In both the cases, the actual $[Mn]$ -content closely approaches the expected equilibrium value in about an hour after the additions, which is rather fairly rapid.

Further evidence of the attainment of manganese reaction equilibrium is borne out in Fig. 6.1.¹⁰ Here the calculated $[\text{Mn}]$ has been found, not from the activities but rather from the number of moles of (FeO) and (MnO) , with the help of the equation,

$$\log K_{\text{Mn}} = \log \frac{n_{\text{MnO}}}{n_{\text{FeO}} \cdot \% [\text{Mn}]} = 10,710/T - 2.877 \quad 6.3$$

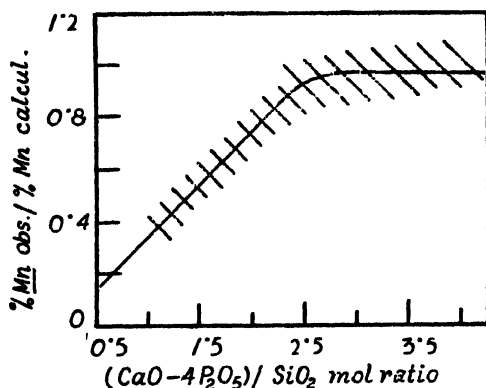


Fig. 6.1—Ratio of observed and calculated residual manganese in basic open-hearth heats as function of lime-silica ratio. (L. S. Darken & B. M. Larsen Trans. AIME, 150, 1942, 87-112).

n_{MnO} and n_{FeO} are the numbers of moles of the two oxides in 100 gm of the slag. Ferric oxide is also taken into consideration by adding 3 times its number of mol to those of FeO. The ratio of $\% [\text{Mn}]$ -(analysed)/ $\% [\text{Mn}]$ -(calculated) is plotted against the basicity ratio $(\text{CaO}-4\text{P}_2\text{O}_5)/\text{SiO}_2$ in mol. It is observed that the Mn-ratio is in the neighbourhood of unity (i.e. the equilibrium is reached) when the basicity ratio is above about 2.4. That the calculation is valid with the mol concentrations, instead of with the activities, only reveals that above a basicity of 2.4, the molecules of FeO and MnO in the slag are substantially free and mol concentrations are, at least, proportional to their activities, or, that the combinations of these oxides with the slag constituents are such that the mol ratios of the two oxides are equal or proportional to their activity ratios. Below a basicity of 2.4, Mn-ratio is below unity, i.e. the calculated values are

much more than those observed. This can only mean (if the equilibrium is reached in reality) that at a lower basicity, i.e. at higher slag silica-contents, the oxides FeO and MnO enter into combination with silica, the effect being the mol ratios are no longer proportional to their activity ratios and the net effect is less pronounced in the case of FeO than of MnO (the activity of MnO is reduced by a greater extent). The fact, however, remains that at higher levels of basicity, the equilibrium is reached in the open-hearth, the observed and calculated ratios being consistently near unity, i.e. the two values are nearly equal.^{10,11}

The significant points that emerge from the above considerations are that (i) the Mn-oxidation is dependent on the (FeO)-activity, i.e. the oxygen potential of the slag (ii) the Mn-reaction is independent of the [C]-content and, therefore, of the oxygen potential of the bath (iii) the Mn-reaction is dependent on the (MnO)-activity. These point out to the fact that the Mn-oxidation can only take place at the slag-metal interface. The metal at the interface maintains the same oxygen potential as the slag. That the equilibrium between the slag and the metal is established in a short period, shows that the rate of oxidation of Mn is fairly rapid. (It may be mentioned here that the oxygen potential of the bath attains that of the slag at low carbon contents, $\sim 0.05\%$). The Mn-oxidation is facilitated by the solubility of MnO in the slag, where it exists in a state of low activity. This is because (and it is another point to the assumption that the reaction occurs at the slag-metal interface) the oxygen content of the bath is not high enough for Mn to react in the bath itself, with the separation of FeO-MnO slag, as can be seen from Fig. 3.9. It is true that, apart from the reaction rate of [Mn] and [O], the rate of transfer of Mn from the metal to the site of the reaction plays a part in the manganese partition between metal and slag; but this postulate becomes more or less unimportant because of the turbulence caused by the vigorous 'boil'.

As has been mentioned above, the [O]-content of the bath is not enough for effecting the oxidation of [Mn]; but on the addition of hot metal (pig iron) during or after the melting, a rapid oxidation of both Mn and Si takes place. Although, the presence of Si should keep [O] at levels lower than in the Si-free melts, yet it is surprising that a considerable amount of [Mn] is

oxidised and goes into the slag. The reason for such a behaviour lies in the fact that the Mn-reaction occurs at the slag-metal interface and also that the (MnO) forms a silicate with the deoxidation product of Si (i.e. silica) and this silicate formation lowers the activity of (MnO), resulting in the transference of Mn from the bath to the slag. As the heat proceeds, this acid silicate dissolves more and more of CaO and MgO, which are strong bases, from the hearth refractories and lime additions. The bases form silicates with the silica. Further, when they begin to dissolve, they displace MnO from the silicates, which results in a considerable increase of the activity or 'free' (MnO) (*cf.* Fig. 4.7), facilitating a Mn-reduction to the bath.

Manganese is a costly metal and every effort must be made to prevent its loss in the slag as far as the steel quality permits and is not affected. Killing¹² and Back¹³ have studied extensively the various conditions which could give the maximum recovery of the element in the metal. The recovery coefficient Q has been formulated as $Q = \text{wt. of Mn in steel} / \text{wt. of Mn in slag}$. It is easy to recognise that, in consideration of the Eq. 3.16 which includes the term (MnO)-slag, the value of Q depends upon the quantities of steel and slag, apart from the effect of chemical conditions.

Killing concludes from his investigations that the quotient Q (and consequently [Mn] in steel) increases :

- (i) if steel is tapped during the maximum Mn-reduction or reversion.
- (ii) if Mn-addition is not too high (1.6—1.8% max.)
- (iii) if the base is neither in excess nor deficient (because in both cases the activity of MnO decreases (*cf.* Fig. 4.7)).
- (iv) if the acid elements in the metal are small; too much of Si, P will give too large amounts of acid oxides on oxidation, which would lower the MnO-activity. They would also increase the slag bulk for maintaining a certain basicity, which means an increased loss of Mn in the slag.
- (v) if Mn is added in metallic form.
- (vi) if the temperature is as high as possible (because the exothermic Mn-oxidation reaction is suppressed as the temperature increases).

Killing in his observations, however, seems to have completely

overlooked the influence of the iron content of slag on the recovery coefficient Q . Schenck⁶ has arrived at almost the same conclusions as those Killing in, however, a little different approach to the problem. He has taken into consideration the effect of the rate and extent of decarburisation as well. Decarburisation requires a definite (Fe) -content of slag which depends upon the temperature, the final [C]-content and the residual composition of the slag. Schenck, further, shows that the lower the [C]-content at which the 'boil' ends, the lower the Q or the utilisation of Mn, provided the temperature, (ΣSiO_2) and (ΣCaO) are the same.

A considerable loss of manganese in the slag is unavoidable in the basic open-hearth practice. Slag weight is also of utmost importance for a good Mn-recovery, since it is not the total amount but wt. per cent of (Mn) in the slag, which controls the equilibrium relations in the Mn-reaction. About 70% of Mn (depending, of course, upon the initial Mn/Si in pig iron) in the non-flush and about 85-90% in the flushing practice are lost in the slag, and this loss naturally increases if the slag weight increases unusually. In an acid slag the (MnO) is bound as silicates and, as such, its activity is lowered, resulting in the escape of [Mn] to the slag. If the slag is too basic, the slag weight as well as the (FeO) increase (Fig. 3.7). Now, from Eq. 3.16, [Mn] is

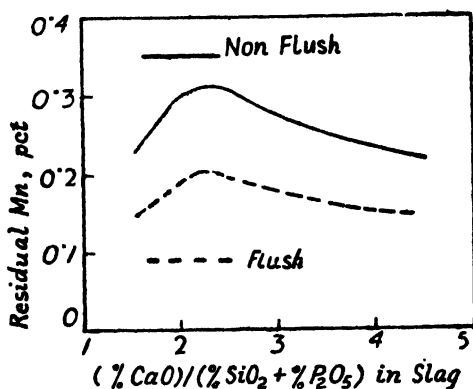


Fig. 6.2—Effect of slag basicity on residual manganese in scrap-hot metal non-flush and high hot metal flush basic openhearth practices. (W. O. Philbrook & F. M. Washburn, Basic Openhearth Steelmaking, AIME, Copyright 1951.)

proportional to $(\text{MnO})/(\text{FeO})$. If (FeO) increases, then naturally $[\text{Mn}]$ would decrease. It has been found, generally, in practice that a ratio $\text{CaO}/(\text{SiO}_2 + \text{P}_2\text{O}_5)$ of between 2.1-2.3 gives an optimum recovery of manganese (Fig. 6.2).¹⁴

Schenck has found that the Mn-recovery decreases at a low carbon finish. As long as carbon is present in a sufficient quantity, it holds the (FeO) -value at a low level. It can be seen in Fig. 3.7 that, for a given basicity, the (FeO) -slag increases as the carbon drops. Therefore, the residual Mn drops as the bath carbon drops (see also Figs. 6.3 and 6.4).

The relative amounts of Mn and Si in the pig iron also play a part. If the initial Mn is high, the residual Mn will also be high, at the same initial Si-content. But with a high initial silicon, more of lime would be necessary to make the required basicity, which would lead to an increased slag volume and the advantage of high manganese input will be lost. The effects of C, Si and Mn on the Mn-recovery are shown in the Fig. 6.3.¹⁴ The curves C and D show clearly the deleterious effect of a high initial Si in the pig iron. The extent of recovery is the same, although the Mn input in D is much less than in C.

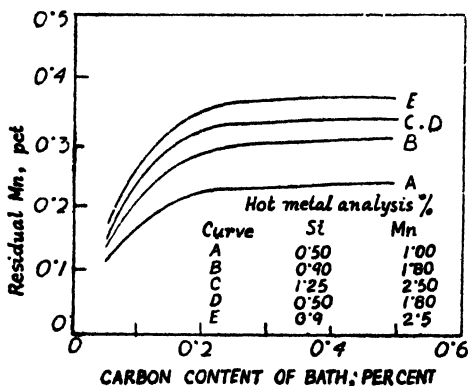


Fig. 6.3—Effect of Mn & Si in hot metal on relation between carbon & manganese contents of bath in basic openhearth non-flush practice. (W. O. Philbrook & F. M. Washburn, Basic openhearth Steelmaking, AIME, Copyright, 1951).

The K_{Mn} value decreases with rising temperature. From the Eq. 3.17, this means that for a constant $(\text{MnO})/(\text{FeO})$ ratio in

the slag, the Mn in the metal must be higher. Thus, an increased temperature facilitates the reduction of Mn from the slag to the bath, other conditions remaining the same. The effect of temperature on the Mn-recovery is clearly shown in Fig. 6.4.¹⁴

Recently, Vom Ende *et al.*¹⁵ have investigated thoroughly, in the laboratory, the manganese equilibrium reaction with slags similar to the basic open-hearth ones. They also find that the reaction, in practice, reaches equilibrium at all stages. The ratio $(\text{MnO})/[\text{Mn}]$ decreases, i.e. $[\text{Mn}]$ increases, as the basicity increases and the manganese reduction from the slag to the metal becomes negligible when the CaO/SiO_2 ratio approaches 2.8.

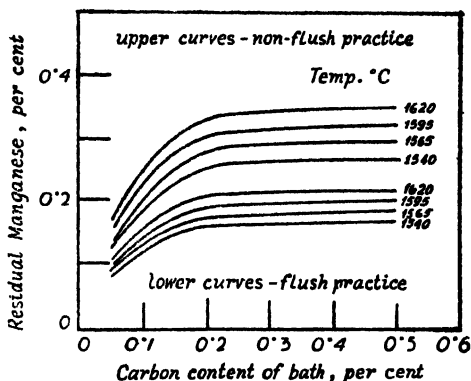


Fig. 6.4—Effect of temperature on residual manganese in scrap-hot metal non-flush (upper curves) and high hot metal flush (lower curves) basic openhearth practice. (W. O. Phillbrook & F. M. Washburn, Basic open-hearth Steelmaking, AIME, copyright 1951.)

At this ratio the slag becomes saturated with lime and tricalcium silicate. The lime-saturation line with $(\text{MnO})/[\text{Mn}]$ ratios at various slag compositions are shown (Fig. 6.5) in the ternary diagram $\text{CaO}'\text{-SiO}'_2\text{-FeO}'$ ($=100$). Actually, these three constituents form about 80% and the rest 20% includes oxides and sulphur.

The investigators conclude that in the region of 'lime-unsaturation',

- (i) with constant basicity and increasing (FeO) , the a_{FeO} increases and, therefore, the Mn suffers an oxidation,

- (ii) with constant (FeO) and increasing basicity, the a_{FeO} decreases and therefore the Mn is reduced from the slag to the metal.

In the 'lime-saturated' region

- (i) an increase in (FeO) means an increase in its activity (*cf.* p. 319) and, therefore, an increase, in the oxidation of [Mn].

An increase in the temperature favours Mn-reduction (since the oxidation reaction is exothermic). Also, the a_{FeO} decreases, inducing further the reduction of the element.

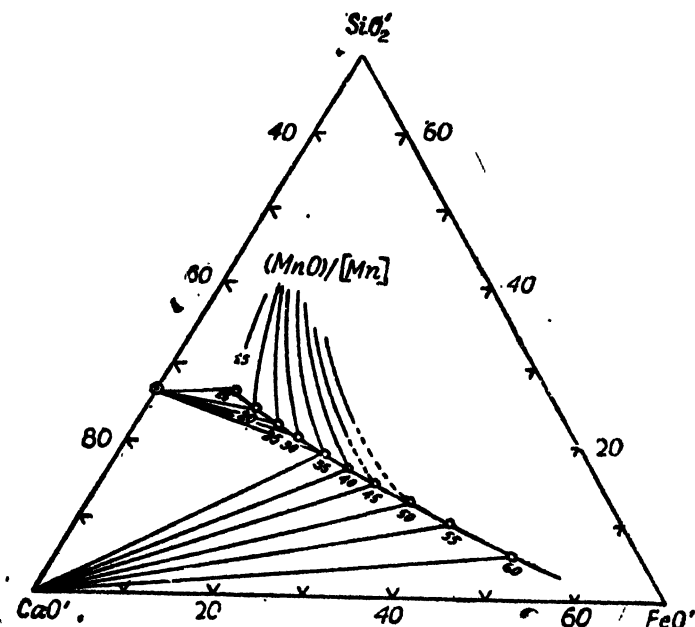


Fig. 6.5—The $(\text{MnO})/[\text{Mn}]$ ratios at various openhearth slag compositions and along the lime-saturation line at 1,650°C. (H. V. Ende, R. Bardenheuer & E. Schurmann, *Stahl und Eisen*, 82, 1962, 1031).

Importance of Manganese in the basic process

The Mn-content of the bath and the (MnO) of the slag partly regulate the (FeO) and, thereby, its activity in the slag and consequently control the oxygen-potential of the bath and, therefore, the rate of the carbon removal. In a Mn-free bath, the flame oxidation of iron would lead to the formation of FeO, which would deliver a large amount of oxygen to the metal according to its acquired activity. This oxygen reacts with the carbon in the metal. The more the amount of [Mn] present in the bath, the more of MnO will be formed according to Eq. 3.15 and, correspondingly, the (FeO)-slag will decrease. Thus, the transfer of oxygen to the bath would be reduced, resulting in a lower rate of decarburisation. The importance of Mn becomes evident, more at the end of decarburisation, in especially low-carbon heats, where a large transfer of oxygen from the slag to the bath has to be prevented or minimised. This can be achieved in the presence of a sufficiently large amount of [Mn].

The Mn-reversion is very useful for judging the correctness, quality and temperature of a heat. An increase of temperature facilitates Mn-reduction. Again, as the temperature increases, more and more of lime goes into solution (up to the saturation limit, cf. Fig. 6.5) and the ratio CaO/SiO_2 rises. According to Vom Ende *et al.*¹⁵ the K_{Mn} -value decreases as the lime-silica ratio increases up to about 2.8, beyond which the K_{Mn} does not vary much. Increasing the temperature and the basicity of slag (up to a certain level) both, therefore, favour the reduction of Mn out of the slag. The presence of carbon in the bath affects the Mn-reduction in so far as it determines the (FeO)-content or its activity in the slag.

Thus, the increase in bath temperature and the slag basicity and the deoxidising effect of carbon all work together in a sense favouring the transfer of Mn from slag to bath. As long as the carbon reaction takes place, the Mn-oxidation is comparatively suppressed. At the end of decarburisation, the oxygen potentials of both the slag and the bath rise, resulting in a decrease of [Mn], if the temperature, however, remains the same.

Manganese reversion is an indirect indication of the cleanness of steel. The cleanness depends, to a great extent, on the final oxygen content of steel. The lower the oxygen, the lower will

be the amount of oxide inclusions formed by the deoxidisers. Now, the oxygen depends upon the iron oxide content of the slag which also regulates the [Mn]-content of the bath. If the decarburisation is ample in volume and intensity, the reduction in the Fe-content of the slag will be considerable, which would lead to a Mn-reversion with simultaneous decrease of the metal oxygen.

The cleanness is also affected by the finely suspended solid oxides, formed from the oxidation of Si and Al contained in pig iron and scrap which do not find time to rise to the surface during the refining period. These oxides can be liquefied in the presence of Mn, depending upon the oxygen in metal. It is easy for liquid droplets to coalesce and grow bigger and come to the top. From Fig. 11.3, the higher the Mn-content, the less is the amount of oxygen required for obtaining liquid oxides.

Thomas or basic Bessemer

The variations of manganese contents with time in the Thomas converter are shown in Fig. 2.3. This element is oxidised, simultaneously with silicon, very rapidly and to a great extent and its oxidation continues until the carbon removal has proceeded far, when the [Mn]-content decreases to 0.1-0.3% from an initial value of 0.6-1.7%. During the changeover or transition marking the beginning of rapid dephosphorisation, the [Mn]-content usually rises and subsequently falls again. In the figure, this rise takes the form of the so-called 'manganese hump', which is more or less pronounced, according to the charge and the temperature.

The oxidation of manganese is given by Eq. 3.15. The initial slag formed is an acid silicate because of the slow rate of dissolution of lime. The oxidation product of manganese, MnO, is bound in a state of low activity in the acid slag, thereby causing an extensive removal of the element. During the continued blow, the temperature rises steadily and the lime dissolves slowly, both favouring the reduction of Mn to the bath. But a part of the dissolved lime combines with P_2O_5 to form phosphate which offsets the favourable effect. Further, there is a build-up of FeO in the slag, since the oxygen supplied by the blast is not entirely consumed by carbon and this (FeO) contributes to the manganese oxidation. Thus, there is overall only a little change in the Mn-concentrations during the decarburisation period.

Active dephosphorisation starts when the carbon reaches $\sim 0.10\%$ and the oxygen-content of steel is $\sim 0.035\%$.¹⁶ At this time of transition, the phosphate of lime and iron oxide in the slag are in such concentrations as to be inside the well-known 'miscibility gap' and the slag exists in two phases, one being the (FeO+MnO)-rich and the other phosphate-rich. The oxide-rich slag is in a state of high (FeO)-activity and maintains a large amount of oxygen in the bath. The oxygen-content seems to be controlled by the (FeO+MnO)-contents of the slag, taking into consideration the dilution by 20-30% of SiO₂ and CaO. A couple of minutes after the transition, i.e. during the after-blow, the high temperature, high iron-oxide and the phosphorus pentoxide all help to flux the lime extensively and the slag composition emerges out of the 'miscibility gap' towards the lime-saturation line (cf. Fig. 8.4). As soon as the slag becomes homogeneous, the high (FeO)-activity of (FeO+MnO)-rich slag assumes the value of that of the phosphate slag and the bath oxygen correspondingly decreases (from the highest value of 0.13 to 0.090%). The prevailing high temperature, the increased MnO-activity of the almost lime-saturated slag and the lower oxygen-potential of the bath — all contribute to the reduction of Mn to the bath and consequently to the formation of the manganese hump. Further blowing oxidises more of iron and leads the slag composition towards the iron-corner and nearer to the gap, which means an increased (FeO)-activity and, therefore, oxidation of Mn, which is both slow and steady.

Although, outside the miscibility gap, the slag is homogeneous yet the increasing activity of (FeO), at higher iron-concentrations of the slag and in the neighbourhood of the gap even for the same (Fe)-content, indicates that the immiscible character of the slag has not been lost. If that is so, then FeO and MnO should behave as in the immiscible oxide-rich phase, i.e. as in a pure FeO and MnO system allowing further dilution of the slag as mentioned above. The manganese equilibrium reaction should follow the trend of the pure FeO and MnO system, which has been found to be the case by various investigators. It has been found that when FeO, MnO and [Mn], as determined from slag and metal analysis, are substituted in Eq. 3.16, a reasonable constant^{1, 17-21} is found which conforms well with the laboratory experiments.^{7, 22}

$$\text{Körber and Oelsen}^7 \text{ have found that } K_{\text{Mn}} = \frac{(\text{MnO}) \cdot 100}{(\text{FeO}) \cdot [\text{Mn}]}$$

changes according to the basicity of the slag, when the oxides are taken as mol fraction or wt. %. They suggest a value of 1200 for the acid and ~ 300 for the basic slags ($\text{CaO}/\text{SiO}_2 > 2$). According to Faust,¹⁷ the value is ~ 250 for the Thomas process. That a reasonable constant is found, by the use of concentration terms in the manganese equilibrium reaction, shows that both FeO and MnO behave ideally in Thomas slags, which is rather surprising in view of the presence of the immiscible region in such slags (*immiscibility indicates a positive deviation from ideality*).

For a true constant, the activity or activity coefficient must be taken into consideration. On this basis Eq. 3.16 can be written as,

$$K_{\text{Mn}} = \frac{a_{\text{MnO}}}{a_{\text{FeO}} \cdot \%[\text{Mn}]} = \frac{N_{\text{MnO}} \cdot f_{\text{MnO}}}{N_{\text{FeO}} \cdot f_{\text{FeO}} \cdot \%[\text{Mn}]} \quad 6.4$$

As an ideal behaviour of both FeO and MnO is doubtful, it is probable²² that, since reasonable constants are found in practice, the activity coefficients of these oxides vary in such a way as to maintain their ratio a constant in Eq. 6.4. It has, however, been found that the actual values of K_{Mn} vary from plant to plant depending upon the steelmaking practice of each unit. This has led to the belief that the manganese reaction does not reach equilibrium in the Thomas process.

Although the manganese reaction may probably attain equilibrium in the presence of lime-saturated phosphate slag as discussed above, recently there is a consensus of opinion that it does not do so in practice.²³ Under a lime-saturated slag, the equilibrium value is given by :

$$\frac{(\text{Mn})}{[\text{Mn}]} \cdot \frac{100}{(\text{Fe})} = 160 \quad 6.5$$

In the Thomas converter, the value 160 is exceeded as the (Fe)-content of the slag increases and ranges between 200-275. This means that more MnO is formed than the equilibrium should permit, although the reverse should be expected since the [Mn]-concentration is progressively diminished as the refining proceeds,

which would rather delay the delivery of manganese to the place of reaction. It is paradoxical that more manganese should be oxidised than what the phosphate slag should do.³³ But this is understandable, if it is assumed that the slag and metal do not attain equilibrium. There are two distinct reaction zones in the converter process. One is the gas (air)/metal and the other the slag/metal interfaces. The air or blast oxidises [Mn] to MnO and a sort of pure FeO-MnO slag is formed around the blast. The phosphate slag, in its turn, should react with this FeO-MnO slag and reduce MnO to the equilibrium [Mn]-value. But it is unable to do so and the phosphorus is answerable for the inability. It has also been found from calculations that the oxygen-content of metal is higher than corresponding to the phosphate slag, but it is lower than corresponding to the FeO-MnO slag in this blast region. It is important to note that, inspite of the great turbulence caused by the blast and consequent thorough inter-mixing, the slag and metal do not attain equilibrium in the Thomas converter. This is borne out by the higher oxygen and phosphorus contents at the end of refining than corresponding to the equilibrium values.

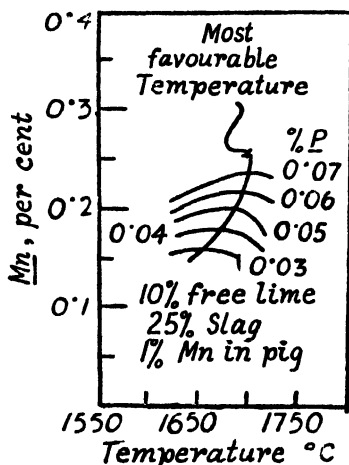
The equilibrium constant K_{Mn} which, otherwise, can also be expressed qualitatively by the distribution ratio between slag and metal, i.e. $(Mn)/[Mn]$, apart from its relation to (Fe)-slag, is dependent upon the

- (1) temperature, i.e. lower the temperature the higher is the ratio, i.e. less of Mn is retained in the bath.
- (2) phosphorus content of steel. Higher the phosphorus, the higher is the [Mn].
- (3) basicity. Higher the basicity the lower is the ratio, i.e. the higher the [Mn].
- (4) manganese in Thomas pig-iron. Higher the manganese in the charge, the greater is the ratio, i.e. more of manganese is oxidised; but naturally the end-[Mn]-content would be higher than with low-manganese-charge.

A good quality Thomas steel is supposed to possess at least 0.2% of Mn. Below this quantity, the cleanness of the steel is affected. Since manganese is a costly material, it is the endeavour of every plant to keep its oxidation to the slag under control.

The manganese efficiency, i.e. the per cent of total manganese charged remaining in the metal, is given by η_{Mn} . The higher the η_{Mn} under certain conditions, the smaller may be the manganese charged for a given end-[Mn]-content and, for a given charge, the smaller will be the manganese necessary for deoxidation.

The slag-iron, as is evident from Eq. 6.5, influences the Mn-content of steel. Lower the (Fe) at the end of the blow which, however, depends upon the temperature and the degree of dephosphorisation, the higher is the manganese. For any desired end-[P], the lower the temperature the lower is the (Fe)-slag necessary for attaining the given [P] (because dephosphorisation is favoured by lower temperatures *cf.* p. 261). However, low temperatures favour Mn-oxidation rather than its reduction. Therefore, for practical purposes, the unfavourable effect of low temperature on Mn-retention is more or less compensated by the favourable effect of low (Fe) at low temperatures. Eichholz and Kootz²⁴ are of the opinion that, for every desired [P]- in steel, there is always an optimum manganese efficiency. Fig. 6.6.²⁴ shows the relation between [Mn] and temperature for different phosphorus contents of steel. The figure is valid for given 'free' lime, amount of slag and manganese in the charge, since all these



[The underlined elements denote their presence in steel.]

Fig. 6.6—Dependence of manganese content of metal on temperature and phosphorus contents.

factors affect the Mn-content of steel. It can be seen from the figure that the highest [Mn] is attainable at lower temperatures if low [P] is desired.

Manganese in steel is dependent on the charged manganese. A high manganese charge has the following disadvantages. It leads to :

- (1) a high oxidation of iron, i.e. high (Fe)-slag;
- (2) a high end- or final-[O] in steel;
- (3) a high manganese loss in the slag;
- (4) a difficulty in controlling the end point because of dense fumes arising at the end. Such fumes are suppressed by adding scrap which may lead to cold heats and low teeming temperatures.

The ratio (Mn)/[Mn] increases with increasing Mn-content of pig-iron and degree of dephosphorisation, but decreases with increasing basicity of slag. The final [Mn]-content decreases with increasing removal of phosphorus. On the other hand, the dephosphorisation is easier, the lower the Mn in the charge, without any corresponding increase in (Fe)-slag.

Reactions of Manganese and Silicon in the Acid Processes

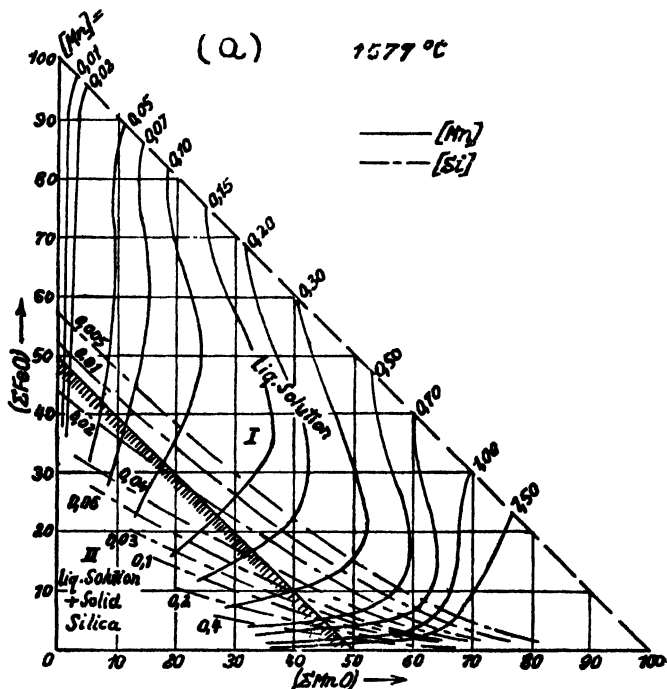
General

Investigations on the equilibrium laws of the manganese and silicon reactions in acid steelmaking are of importance for understanding the transference of these elements from metal to slag and *vice versa*, although it is doubtful whether the equilibrium between slag/metal is reached at all. The simplest slag which is in equilibrium with iron, containing Mn and Si, is FeO-MnO-SiO_2 . At steelmaking temperatures the slag is a liquid and homogeneous silicate up to about 50% silica which is the saturation limit as already explained (cf. p. 85 and Fig. 3.42). At higher silica contents, a heterogeneous mixture of liquid silicate and solid silica is formed. The viscosity increases greatly as the solid silica increases and the high viscosity plays an extremely important role in the acid open-hearth process. The limited solubility (50-60%) of silica in the acid slag enables us to melt pig iron in the acid process over a silica lining; otherwise, the lining would not only erode quickly but the entire Si-Mn reactions would be affected, as

we will see later. In practice, the acid slag is not a pure iron-manganese silicate but contains lime and alumina, these being either deliberately added or are dissolved from the lining. Lime increases the solubility of silica (to about 70%). It increases and the alumina decreases the viscosity of the slag. It should, however, be borne in mind that apart from Mn and Si, carbon is always present in the bath. It is the most important constituent that exhibits a reducing action on the oxides and, as we will see, this reaction mainly determines the direction of the process.

In order to have a better appreciation of acid steelmaking, the reader may refer, before proceeding further, to the equilibrium relations given in the Fe-Mn-O, Fe-Si-O, Fe-Mn-Si-O, Fe-Mn-Si-C-O systems and the FeO-MnO SiO₂ slag and its variation with CaO, Al₂O₃ etc. In the following sections the equilibrium relations are discussed further and, thereafter, the reactions of Mn and Si in acid process will be taken up.

Without going into the works of various earlier investigators, the



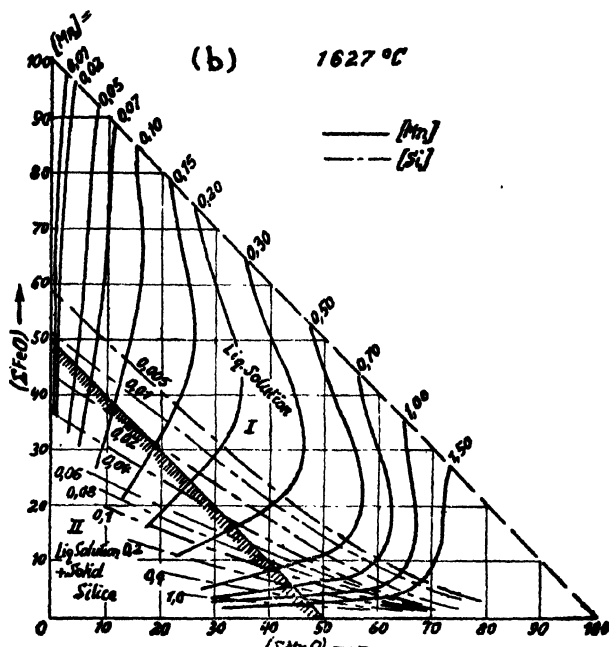


Fig. 6.7—Equilibrium concentrations of Mn & Si in liquid iron under FeO-MnO-SiO₂ slags at (a) 1,577°C & (b) 1,627°C. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

results of Schenck and Brüggemann²⁵ on practical works measurements are discussed here. They have calculated the 'free' concentration of (FeO), (MnO) and (SiO₂) in the acid slags, assuming the validity of Körber-Oelsen's K_{Mn} and L_{FeO} (deduced for pure FeO-MnO slags) in acid processes. They have represented graphically the Mn and Si contents of the metal when in equilibrium with acid slags. In acid slags, the sum $(\Sigma \text{FeO}) + (\Sigma \text{MnO}) + (\Sigma \text{SiO}_2) = 100$, which enables us to represent lines of equal [Mn] and [Si] concentrations in a triangular diagram as functions of (ΣFeO) and (ΣMnO) , the remainder being silica. Figs. 6.7 (a) & (b) are such diagrams⁶ for temperatures of 1,577° and 1,627°C, the area marked II being the region of the presence of solid silica.

Area II, on the left-hand side of the triangles, is the region where the slag is super-saturated with silica and, therefore, the

slag is heterogeneous with two separate phases : liquid slag solution and solid silica. The composition of liquid slag in the heterogeneous system is given⁶ by joining the actual slag composition with the lower left-hand corner and extending the line to where it meets the boundary with *I*, the area of liquid silicate. The [Mn] and [Si] concentrations would correspond to the slag of this new composition. As for example, in the schematic diagram Fig. 6.8, the liquid slag composition is given by *X* where the extension of the join of corner *Z* and the actual slag composition *Y* meets the silica saturation boundary.

A study of Schenck's diagrams⁶ reveals the following :

- (1) Addition of lime changes the equilibria involved, resulting in an increase of [Mn] and decrease of [Si].

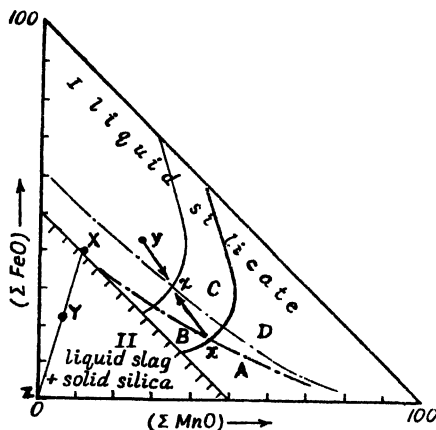


Fig. 6.8—Effect of changes in acid slag composition on residual Mn & Si, (Schematic).

- (2) For constant values of (ΣFeO) and (ΣMnO) , the replacement of silica by neutral components (like alumina) leads to a decrease in [Si] and to a slight increase of [Mn].
- (3) Increase of temperature causes an increase of both [Mn] and [Si], for the same slag composition.

The findings of Schenck and Brüggemann, based on actual steelmaking data, are useful for practical purposes. Körber and Oelsen,²⁶ during their experiments on equilibrium with the metal

containing Mn and Si under a silica-saturated ternary FeO-MnO-SiO₂ slag, have reached the conclusion that such equilibria regarding Mn and Si can be expressed simply by :

$$\log K_{\text{Mn}} (\text{acid}) = \log \frac{(\Sigma \text{FeO})}{(\Sigma \text{MnO})} \cdot [\text{Mn}] = -7,940/T + 3.172$$

$$\log K_{\text{Si}} (\text{acid}) = \log (\Sigma \text{FeO})^2 \cdot [\text{Si}] = -19,057/T + 11.101$$

The K_{Si} equation does not include SiO₂, since its activity in a silica saturated slag is constant and is, therefore, included in K_{Si} .

The application of Körber-Oelsen's equilibrium relations in works melts gives much lower values of [Mn] and [Si] than found by analysis; whereas, that of Schenck and Brüggemann, gives better results although the discrepancies are such as cannot be neglected. The carbon reaction and slag viscosity are supposed to be responsible for the non-applicability of the equilibrium relations to practical heats. More concordant results of Schenck and Brüggemann are probably due to their derivation of the relations from practical steelmaking data.

Before going over to the reactions of Mn and Si in presence of carbon and thereafter to the actual acid processes, it may be worthwhile to discuss here how the pure systems Fe-Mn-O and Fe-Si-O are affected by FeO-MnO-SiO₂ slags, with and without impurities like lime and alumina.²⁷ For Mn-reaction, the equilibrium index K'_{Mn} is given by :

$$K'_{\text{Mn}} = \frac{(\text{FeO})}{(\text{MnO})} \cdot [\text{Mn}]$$

In the pure system, the value of K'_{Mn} at 1,540°C is 0.23 (Eq. 3.16). But with the introduction of SiO₂ in the slag, the constant changes and it is about 0.05 in the region of 0.01-0.1% [Mn]. Evidently SiO₂ affects the activities of both FeO and MnO and that, too, to an unequal extent. The decrease in K'_{Mn} -value is due to the fact that as SiO₂ is introduced to the pure FeO-MnO system, the activity coefficient of FeO falls at a slower rate than that of MnO. The relation between true equilibrium constant K'^{*}_{Mn} and the K'_{Mn} is given by :

$$K'^{*}_{\text{Mn}} := \frac{a_{\text{FeO}} [\text{Mn}]}{a_{\text{MnO}}} = [\text{Mn}] \cdot \frac{(\text{FeO})}{(\text{MnO})} \cdot \frac{\gamma_{\text{FeO}}}{\gamma_{\text{MnO}}} = K'_{\text{Mn}} \cdot \frac{\gamma_{\text{FeO}}}{\gamma_{\text{MnO}}}$$

$$\text{or } K'_{\text{Mn}} = K'^*_{\text{Mn}} \frac{\gamma_{\text{MnO}}}{\gamma_{\text{FeO}}}$$

Evidently K'_{Mn} would decrease if γ_{FeO} decreases more slowly than γ_{MnO} .

Additions of SiO_2 , Al_2O_3 , CaO , all decrease the K'_{Mn} -value *vis-a-vis* the value for pure FeO-MnO system. Silica brings the value down to about 0.05-0.1, whereas alumina and, more so the CaO bring it to the order of 0.01. Such additions are, therefore, expected to decrease the ratio $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$. From the activity diagrams, Figs. 4.9 and 4.6, of MnO and FeO , it is clear that the value $\gamma_{\text{MnO}} = 1$ (for pure FeO-MnO system) is lowered to about 0.15 by SiO_2 and still lower by lime and alumina. In the case of γ_{FeO} , it is lowered to 0.75 when SiO_2 is added to FeO and this coefficient increases on further addition of MnO , CaO or Al_2O_3 . This happens because the Mn-silicate possesses a stronger bond than the Fe-silicate . These additions may be deemed to be capable of driving out the FeO from its silicate, thereby increasing its activity. It follows, for example, that the lime lowers

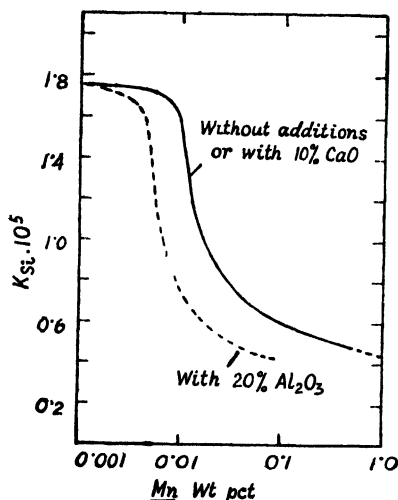


Fig. 6.9—Dependence of the equilibrium constant $K_{\text{Si}} = [\text{O}]^2 \cdot [\text{Si}]$ in liquid iron under silica saturated FeO-MnO-SiO_2 slags on the manganese content of metal. Effects of lime & alumina impurities are also shown. (H. Schenck & G. Wiesner, Archiv f.d. Eisenhuettenwesen, 27, 1956, 8).

the K'_{Mn} -value and makes the reducibility of MnO more difficult.

The silicon reaction in the pure Fe-Si-O system²⁷ is given by Eqs. 3.20-3.23. If MnO is brought into the FeO-SiO₂ slag in the above system, there is a sharp fall of K_{Si} , from $1.74 \cdot 10^{-5}$ at 1,540°C to about a quarter of its value. Since MnO in slag would introduce [Mn] in the metal, a similar lowering of K_{Si} is seen when it is drawn against % [Mn] (cf. Fig. 6.9). Although the addition of about 10% CaO to the new system does not further alter K_{Si} much, yet 20% Al₂O₃ effects a larger diminution of the K_{Si} -value. Such a lowering means a lower [O]-content in the metal than in the case of pure FeO-SiO₂ system. At the first sight, one may ascribe it to dilution of FeO-SiO₂ by MnO resulting in a lower FeO-content of the slag. But such a dilution is caused by Al₂O₃ or CaO also when added to the pure FeO-SiO₂ system, but the K_{Si} and, therefore, the [O]-contents are not lowered by such additions. The decrease of K_{Si} by increasing amounts of [Mn] or (MnO) shows that the smaller [O]-content is not correspondingly compensated by a further reduction of Si from slag to metal. One can only imagine that the activity of oxygen decreases slower than its concentration. Similar phenomenon can, of course, be ascribed to Si as well. The causes of this peculiar phenomenon are still unknown.

The equilibrium relations of Mn and Si, alone or together, are affected by the presence of carbon which is almost invariably present in the steel bath. The influence of carbon on slag-, Si and O-isotherms has already been discussed on pp. 92-95.

In short, if the [C]-content lies above the equilibrium value, it would reduce Mn and Si from the slag until its equilibrium value is reached; if it lies below, then CO will not be formed, rather it will be reduced to C by Fe, Mn, Si. A decarburisation may, however, take place if the partial pressure be lowered, e.g. by melting under low pressures or in admixture with foreign gases. Temperature has a considerable influence on the equilibrium isotherms. At lower temperatures and definite [Mn] and [Si]-contents and slag composition, the C-content in equilibrium is higher than at higher temperatures.

The inferior reducing action of carbon on SiO₂ and silicate slags with decreasing temperature becomes more clear when the

deoxidising action of carbon is compared with that of Si and Mn for 1,500° and 1,600°C, as shown in Fig. 3.21. In the figure, [Mn] is drawn against [O] when enough silicon is added to the melt so that a silica-saturated Fe-Mn-silicate just starts separating out; in such a case Mn has its maximum deoxidising action. The figure brings out clearly the suppression of silicon oxidation and retention of Si in the melt at higher temperatures.

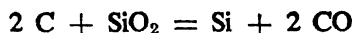
Acid open-hearth²⁸

In the actual open-hearth practice, the laboratory equilibrium experiment results (*cf.* p. 92) are not directly applicable. This is due to the inhibition of C-O reaction caused by lack of nucleation facilities for CO evolution. The resulting sluggishness of carbon reaction affects the silicon and manganese reactions between the metal and slag. This will be clear from the data of an actual open-hearth practice and the corresponding equilibrium values (from Fig. 3.20), based on the same manganese contents in both the cases (see Table 6.1).²⁸

TABLE-6.1

<i>Constituents</i>		<i>Actual Open-hearth heat %</i>	<i>Equilibrium %</i>
Steel	C	1.08	0.03
	Si	0.18	0.02
	Mn	0.06	0.06
Slag	FeO	31.3	32
	MnO	11.7	18
	SiO ₂	57.0	50

Although the equilibrium value of Si in metal in contact with the slag is 0.02%, in actual practice the silicon reduction is to an extent of 0.18%. Since the slag and the metal are in direct contact and both are stirred by the boil, the possibility of Si-reduction from the slag is rather remote. But at the hearth surface, where almost pure silica is in direct contact with high carbon metal at high temperatures, it is possible for carbon to reduce the silica :



This reaction should give much higher silicon than obtained in practice. It does not so happen because the silicon thus reduced diffuses to the slag/metal interface where it is oxidised to silica

and is incorporated in the slag. Thus, during the later period of acid open-hearth steelmaking when the furnace is hot, there is a continuous transference of Si from the hearth to the slag *via* the metal. The final silicon in steel will depend upon the viscosity and iron oxide activity of slag, the temperature as well as the carbon content of the metal.

The viscosity of acid slags plays a great role in the oxidation processes involved. It will be seen from Fig. 3.20, that a (FeO) content of 10% should suffice for the required oxidising effect, whereas in actual practice the slag contains 30% (FeO) and still the carbon reaction may cease and the boil stop during the process while carbon is high. This can obviously be due to high slag viscosity caused by the incorporation of solid silica in the already silica-saturated slag. The same oxidising effect can be obtained with less than 10% (FeO) if lime is added, which increases the saturation value of silica from 50-60% to 70-75%.

It is doubtful whether [Mn] and [Si] reach equilibrium with the slag in acid open-hearth. However, Schenck has forwarded diagrams,⁶ based on actual steelmaking data, depicting Si and Mn in metal for different temperatures and slag compositions (Fig. 6.7). These are valid for silica-saturated FeO-MnO-SiO₂ slags. He has also given figures for such slags containing 10% of neutral constituents, where [Si] and [Mn] are somewhat lower. The influence of temperature is such that, at higher temperatures, the metal shows higher [Si] and [Mn] values for the same slag compositions.

The effect of slag compositions on metal can be ascertained from the consideration of Fig. 6.7. Fig. 6.8, which is a schematic diagram of the same figure, shows the [Mn] and [Si] concentrations in bold lines and the thin lines show their concentrations after an alteration in the slag composition. The newer values are smaller than given by bold lines, as can be gathered from a comparison with Fig. 6.7. The bold lines divide the figure in four zones—A, B, C and D.

Suppose, at a given temperature, additions are made to a slag of composition *x* in equilibrium with the metal so that the new composition is given by *y* (area C). Immediately, as the equilibrium is disturbed, the bath and slag would react so as to shift the metal composition in the direction of *y*. Again, the slag

reaction would tend to shift y towards x . Ultimately, the equilibrium will adjust itself, say at a point z , which lies on the straight line xy . Since, at z both $[\text{Si}]$ and $[\text{Mn}]$ are lower than at x , it is clear that the shifting of slag composition into the zone C has resulted in the oxidation of both the elements. A similar argument for other areas leads us to the conclusion that additions which shift the slag composition into

area A	result in increase of $[\text{Si}]$	and increase of $[\text{Mn}]$
„ B	„ „ „ „	$[\text{Si}]$ and decrease of $[\text{Mn}]$
„ C	„ „ decrease of $[\text{Si}]$	„ „ „ $[\text{Mn}]$
„ D	„ „ „ „	$[\text{Si}]$ and increase of $[\text{Mn}]$

The distance of z from x would determine the final composition of metal. The smaller the amount and the change of composition of the slag, the shorter will be the distance of z from x .

Addition of iron ore to the slag would take its composition towards area C , involving oxidation of both Si and Mn ; whereas, on the addition of manganese ore, the direction would be towards D , resulting in an oxidation of $[\text{Si}]$ and reduction of MnO . If the Mn -ore contains lot of iron oxide or if the state of oxidation of Mn -ore is higher, the iron oxide added or formed would counter-act the reduction of MnO . Additions of sand or siliceous ores or the reaction of the metal with the hearth would displace the slag composition towards B , involving in an increase of $[\text{Si}]$.

Pure silica of the hearth is always in a state of non-equilibrium with the steel bath. Therefore, the hearth will endeavour to attain a composition which would tend to be in equilibrium with steel. This can only happen by the incorporation of FeO from steel and of Mn as MnO (Mn reacting with silica and forming MnO). The thin film of slag, thus formed, may penetrate the lining in part, and the remainder rising to the top as droplets. This process plays the part of automatic deoxidation so well-known for acid open-hearth steel.

When the hearth surface is coated with such metallic oxide films, the role played by silica lining will be much diminished. It is for this reason and also for increasing the hearth life, that after every cast the hearth is fettled with sand and the surface renewed.

The role played by manganese in modern American acid open-hearth practice will be clear from discussions on pp. 51 and 175.

Acid Bessemer

The reader may refer to pp. 23 and 350.

Oxygen Processes¹⁹

In contrast to Thomas process, the manganese distribution ratio $(Mn)/[Mn]$ in top-blown oxygen process is much lower, especially in the beginning when the metal and the slag are rich in carbon and iron oxide respectively. This retardation of manganese oxidation is due to the sluggish transport of manganese atoms to the place where the slag is formed and the oxygen diffuses in the metal. At the end of the blow also, the distribution ratio is lower than in the Thomas process. This is understandable because in the latter process, the oxygen comes directly in contact with the constituents of the metal during the after-blow period when the carbon reaction is absent. In the top-blown process, the carbon reaction continues to the end (since dephosphorisation precedes decarburisation) and, therefore, the manganese oxidation is controlled only by the phosphate slag. As long as sufficient carbon is present in the metal, the oxygen cannot build up in the zones around the blast. The ratio is also low, even lower than the equilibrium values, in the case of top-blowing with simultaneous secondary bottom-blow.

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THE REACTIONS OF CHROMIUM

General

In the presence of oxygen, chromium may form the following three oxides : CrO , Cr_2O_3 , CrO_3 . The dissociation pressure of CrO_3 is very high and even below $\sim 300^\circ\text{C}$ it dissociates into Cr_2O_3 and O_2 . It is presumed that, in acid slags, the element is present mainly as CrO with very little of Cr_2O_3 . In basic slags the latter is predominant.

The behaviour of chromium in the steelmaking processes is similar to that of manganese. The latter is, however, oxidised more easily. Both Mn and Si are capable of reducing chromium oxides and, therefore, act as protectives against the Cr-oxidation. As long as sufficient Mn and Si remain in the metal bath, the Cr-oxidation is delayed and accelerates only after their removal. The effect of temperature is such that, for the same oxygen-content of iron or for the same (FeO) -activity in the slag, the Cr-oxidation increases with falling temperature.

Since chromium is a valuable alloying element, its retention in the bath is desirable as far as possible. But there are circumstances which necessitate its removal from steel, when it accompanies the pig-iron produced from chromium-bearing ores. In either case, a knowledge of the behaviour of chromium in the slag-metal reactions is most helpful. In short, the oxidation-reduction of chromium depends upon the temperature, the composition of the metal and slag, and also upon the amount of slag.

Acid Processes

Körber and Oelsen¹ have carried out experiments with molten iron under liquid iron-silicate slag in silica crucibles to which ferro-chrome was added. A large amount of chromium is thereby oxidised and goes to the slag, with the simultaneous reduction of (FeO) from the slag. The results are shown in Fig. 7.1² for $1,600^\circ\text{C}$. The curves *I* and *II* show the decrease of (FeO) and increase of (Cr) in the slag with increasing $[\text{Cr}]$ in the metal.

The silica content of the slag, however, hardly suffers any change as (FeO) is replaced by chromium oxide (curve III). It can be seen from the dotted curve V (valid for Mn only) that, in comparison with Mn, the reducing power of Cr for (FeO) is much less, e.g. 0.4% Mn reduces (FeO) to the same extent as $\sim 10\%$ Cr; these amounts of the two elements reduce individually 0.1% Si from the slag (and the crucible) as shown by the curves VI and IV. The results indicate that Mn is about 27 times more active than Cr.

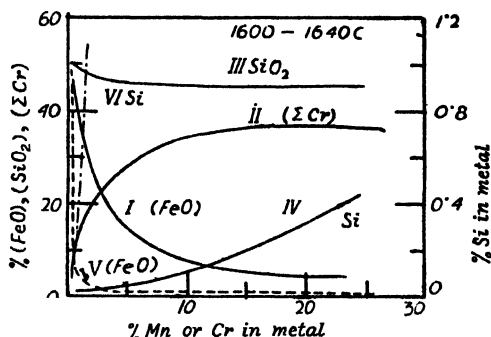


Fig. 7.1—Equilibrium between iron-chromium melts, iron-chromium silicates & solid silica at 1,600-1,640°C. The dotted lines V & VI show the action of manganese in the same sense. (F. Körber, Stahl und Eisen, 56, 1936, 435).

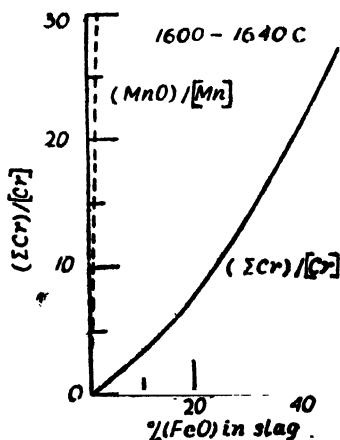
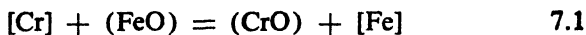


Fig. 7.2—Oxidation of chromium by acid slags at 1,600-1,640°C. Dotted line shows the (MnO) / [Mn] values for comparison. (F. Körber, Stahl und Eisen, 56, 1936, 436).

The similarity of the behaviour of Cr, Mn and Si in acid processes and other considerations have led Körber² to believe that CrO is the stable oxide in liquid acid slags. On this assumption, the Cr-oxidation reaction is given by :



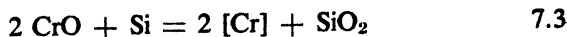
The equilibrium constant can be written as :

$$K = (\Sigma \text{Cr}) / ([\text{Cr}] \cdot (\Sigma \text{Fe})) \quad 7.2$$

A straight line obtained from the plot of the above values shows that the chromium distribution ratio is directly related to the (Fe)-content of the slag. Others^{3,4} are also of the opinion that most of the chromium in acid slags, in equilibrium with liquid steel, exists as CrO and only a little as Cr₂O₃.

The ratio $(\Sigma \text{Cr})/[\text{Cr}]$ rises as the (FeO) in acid slags (containing even CaO, apart from MnO) increases (Fig. 7.2²). The ratio is only unity at (FeO) \sim 3% but increases to 28 at (FeO) \sim 50%. For comparison, the much higher ratio of Mn-oxidation, under more or less the same conditions, is shown by the dotted line in the figure.

Since (FeO) decreases as Si and Mn in the metal increase, it follows that the oxidation of chromium is inhibited by such increases. But the condition becomes different when the slag is reduced by additions of ferro-silicon during the reducing period in electric furnaces producing high-chromium steel. The chromium distribution ratio decreases as the temperature rises, especially above \sim 1,600°C. This beneficial effect is somewhat counteracted by the opposing tendency of silicon being reduced from the slag, i.e. the less susceptibility of Si-oxidation at high temperatures with the consequent failure of the element to exert its fullest influence to reduce the chromium from the slag or protect it from oxidation. At lower temperatures, silicon should help the reduction of Cr from the slag; but difficulties are created at low temperatures because of the retarded reaction rate, as was faced by Hilty⁵ in reducing the valuable element from acid slags in the electric furnace. The relevant equation is :



The reaction is exothermic and, therefore, Cr-reduction is favoured with falling temperature. The reaction can be made to proceed to the right if the silica activity of the slag is decreased by increasing the basicity to a limited extent.

Basic Processes

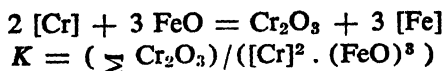
As in the acid processes, the chromium distribution ratio in the basic processes also is profoundly affected by (FeO)-slag and temperature. High (FeO) and low temperature both increase the Cr-oxidation. The ratio is, however, much larger in the basic (~ 2 times)⁶ than in the acid open-hearth process. This suggests that Cr_2O_3 is acidic in nature, at least, in basic slags and its combination with lime (formation of stable $2 \text{CaO} \cdot \text{Cr}_2\text{O}_3$ being envisaged, supported⁷ by petrographic examination) reduces its activity which induces further transfer of the element to the slag. Lapizki⁶, Bardenheuer⁸ and Hauck⁹ all agree to the increased loss of chromium in highly basic slags. Yavoiskii and Dzemyan⁸ find no influence of the basic slag on chromium recovery. Grant *et al*¹⁰ have, however, shown that Cr_2O_3 behaves as a base in basic slags and that the beneficial effect of the basic slag on chromium recovery is very small.

As already indicated, the (FeO)-slag plays a vital role and its increase leads to a rapid and considerable oxidation of chromium. According to Lapizki⁶, the distribution ratio, in both basic open-hearth and electric furnaces, is given by:—

$$(\Sigma \text{Cr})/[\text{Cr}] = 0.136 \sqrt{(\text{FeO})^8}$$

Grant *et al*¹⁰ suggest that the primary role is played by the (FeO) and the temperature; the slag basicity assumes secondary importance. Below $\sim 30\%$ (FeO), it plays the leading role, whereas above this amount the temperature assumes the controlling factor regarding the chromium reaction. The recovery increases substantially, especially above $1,600^\circ\text{C}$.

The relation between the chromium distribution, temperature and (ΣFeO) has been studied by Plöcklinger¹¹ in basic open-hearth melts containing varying amounts of carbon. Assuming the following reaction to take place,



Plöcklinger has found straight line relations as shown in Fig. 7.3. K at $1,600^{\circ}\text{C} = 0.0144$. The figure compares the manganese oxidation as well. The great influence of high temperatures and low (FeO) on the chromium reaction is clear.

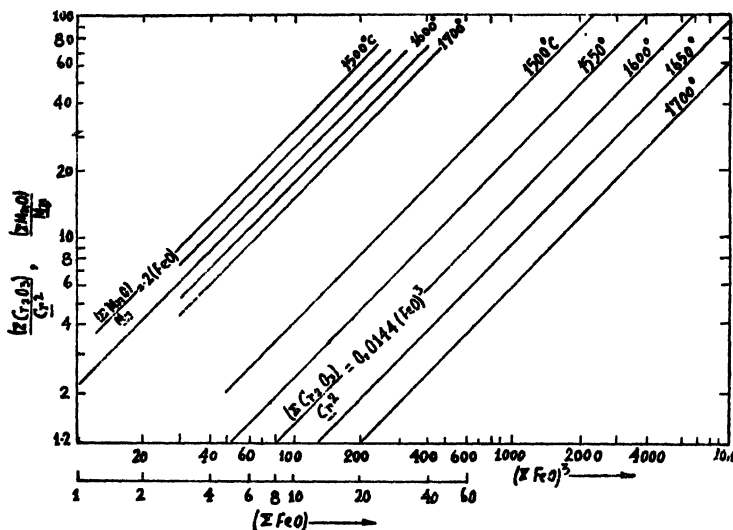


Fig. 7.3—The temperature dependence of chromium and manganese oxidation under basic slags. (F. Plöcklinger, Archiv f.d. Eisenhuettenwesen, 22, 1951, 283).

[The underlined elements denote their presence in steel]

Malcor¹² assumes the same reaction and suggests $K' = 0.069$ in the following equation :

$$K' = [\text{Cr}] \cdot (\text{Fe})^{\frac{3}{2}} / (\sum \text{Cr})^{\frac{1}{2}}$$

Chromium oxidation is inhibited in the presence of large amounts of carbon, since the Cr-activity is lowered by carbon. As the refining proceeds and carbon decreases, the Cr-oxidation increases simultaneously. It is higher, the lower the temperature and the carbon-content reached. For making high chromium steel, it is usual to reduce the slag and, therefore, the Cr-oxide with ferro-silicon during the reducing period in the electric furnace, in order to recover 80-90% of chromium from the slag. Although the high temperature helps in the recovery, it is endea-

voured to arrive at the 'reducing period' with a low temperature.¹³ This is because, the silicon oxidation reaction is highly exothermic and the intense heat evolved inhibits the silicon oxidation and, thus, the slag reduction is suppressed. When the temperature is high, it is best to use low silicon ferro-alloy so that the large amount of metallics would itself cool down the slag. In making stainless steel, Rassbach and Saunders¹³ have found that during the reducing period, the chromium recovery increases with rise in basicity.¹⁴ But at $(\text{CaO} + \text{MgO})/\text{SiO}_2 = 1.4-2.2$ the slag is no longer in equilibrium and the reduction recovery more or less stops,¹⁵ perhaps because of the increased viscosity of the slag. At a basicity ratio of 1, the chromium in the slag is about 10% and it is about 5% at a basicity of 1.4, above which there is no further reduction.

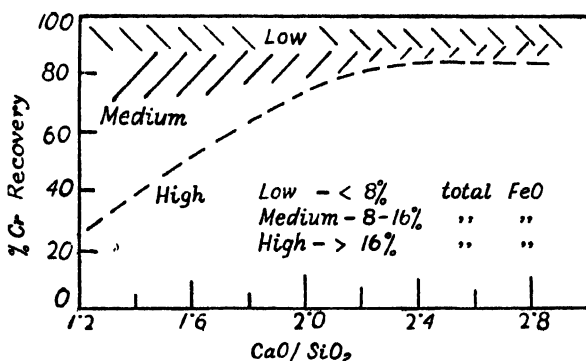


Fig. 7.4—Influence of iron oxide content and basicity of slag on chromium recovery. (Basic Openhearth Steelmaking, p. 240, AIME, Copyright 1951).

As in the case of manganese, the recovery of chromium in the basic open-hearth is facilitated by (a) a high slag basicity (b) a high temperature (c) a low (FeO)-slag, or high bath carbon, as a corollary (d) a low slag volume. Below CaO/SiO_2 of 2.0-2.2, the adverse effect of the high (FeO)-slag is enormous as can be seen from Fig. 7.4. The figure has been computed by Soler¹⁶ from the oxidising slags at melt down in the electric furnace, but it may be useful, as a qualitative guide rather than quantitative, elsewhere.

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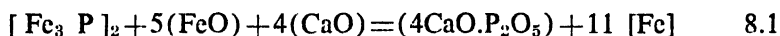
CHAPTER VIII

THE REMOVAL OF PHOSPHORUS

General

The presence of phosphorus in steel, except in certain special grades, is detrimental to its quality and therefore has to be eliminated to below a specified amount. The removal of phosphorus takes place by oxidation, the product of the oxidation, P_2O_5 , being held in combination with basic constituents in the slag. The extent of the removal is governed by the equilibrium condition which is characterised not only by the metal and slag compositions but also by the temperature. We have already discussed all these aspects on pp. 95-114.

We have seen that iron oxide by itself is unable to eliminate phosphorus from iron to any great extent. In practical steel-making, lime is used as a base strong enough for the purpose. Schenck & Riess^{1,2} put forward the following equation for phosphorus equilibrium, assuming $4CaO.P_2O_5$ to be rather more stable than $3CaO.P_2O_5$ or any other phosphate present in the basic open-hearth and basic bessemer steelmaking slags :



$$\log K_p = \log \frac{[\Sigma P] \cdot (FeO)^5 \cdot (CaO)^4}{(\Sigma P_2O_5)} + 0.06 (\Sigma P_2O_5) =$$

$$\frac{-51,800}{} + 35.05 \quad 8.2$$

They introduced $[P]$ as the first power for finding a reasonably 'nonvariable' equilibrium constant. Fe_3P as such has no theoretical significance. In the above equation, (FeO) and (CaO) are 'free oxides' and are derived from the extensive charts prepared by Schenck² for various slag compositions, at different temperatures, by inter- and extrapolations. They are, further, of the

opinion that phosphates other than that of calcium do not have influence on the dephosphorisation because of their lower stability or concentrations in steelmaking slags (except that MnO has a slight favourable effect). The equation, though empirical in nature, can be applied to practical steelmaking with a greater degree of safety than other more theoretical approaches.

An example of Schenck's method of phosphorus calculation is given below:

The phosphorus content of steel is required when a bath at $1,627^{\circ}\text{C}$ is in equilibrium with a slag composition; $(\Sigma \text{Fe})=10$, $(\Sigma \text{MnO})=10$; $(\Sigma \text{CaO})=45$; $(\Sigma \text{SiO}_2)=20$; $(\Sigma \text{P}_2\text{O}_5)=3$; Now from Eq. 4.1, $(\Sigma \text{CaO})=45-1.57 \cdot 3.0=40.3$ which gives, by interpolation from Fig. 4.2, the free oxide concentrations

$$(\text{CaO}) = 27.5 \text{ and } (\text{FeO}) = 5.8$$

At $1,627^{\circ}\text{C}$, $\log K_p = 7.79$. Therefore,

$$\begin{aligned} \log [\text{P}] &= \log K_p + \log (\Sigma \text{P}_2\text{O}_5) - 5 \log (\text{FeO}) - 4 \log (\text{CaO}) \\ &= 7.79 + 0.477 - 5.0 \cdot 763 - 4.1 \cdot 439 - 0.063 \\ &= -1.48, \text{ or } [\text{P}] = 0.033. \end{aligned}$$

In works practice, as will be seen subsequently, the phosphorus equilibrium is reached or nearly approached in both the basic converter and the open-hearth. Various considerations lead us to assume that phosphorus removal from the metal is facilitated by :

- (a) low temperature
- (b) high basicity or lime content of the slag
- (c) high ferrous oxide activity or iron content (ΣFe) of the slag
- (d) low P_2O_5 activity or $(\Sigma \text{P}_2\text{O}_5)$ content of the slag
- (e) low silica content (ΣSiO_2) of the slag
- (f) high (ΣMnO) —content of the slag
- (g) high slag volume or double or multiple slagging

The above mentioned conditions for an effective dephosphorisation are known to modern steel melters. We may now discuss briefly each item :

(a) Phosphorus removal is aided by low temperatures. In the 'puddling process' of steelmaking, although the phosphate in

slag is merely present as an iron compound which is not very stable, yet a certain degree of dephosphorisation is attained in fact because of the comparatively very low temperatures involved. In the actual open-hearth and converter practice, the temperature attained is in the neighbourhood of $1,600^{\circ}\text{C}$ which leaves little scope for adjusting it to our advantage. In the basic open-hearth, a compromise has to be made, since high temperatures favour sulphur removal. In the basic converter, the influence of the temperature is considerable and suitable coolants are used to keep it as low as practicable. However, in the laboratory experiments, the influence of the temperature is not to such a degree as is discernible in practice.³

(b) Lime binds P_2O_5 (an acid oxide) in a state of low phosphate activity by forming calcium phosphate. A high lime activity and low phosphate activity will aid phosphorus removal. For an efficient dephosphorisation, the lime should be liquid and for its highest activity the slag should be in equilibrium with pure lime which is solid at steelmaking temperatures. Thus, a liquid slag saturated with lime would be most advantageous for the purpose. It is, however, not the actual lime content that counts but rather the 'available lime' or 'excess lime', which is left after the formation of phosphates and silicates. In practice, it is usual to measure it by the basicity ratio, i.e. CaO/SiO_2 or $\text{CaO}/(\text{SiO}_2 + \text{P}_2\text{O}_5)$, whose increase facilitates phosphorus removal. A liquid lime slag should be obtained as early as possible for a rapid dephosphorisation. Phosphorus removal in Thomas converters is considerably delayed because of the late solution of lime in the slag, which occurs only in the 'after-blow' period.

(c) A high state of oxidation of the slag and, therefore, of the metal is essential for an efficient dephosphorisation. Since the activity of ferrous oxide of the slag is a measure of the oxygen potential of the bath, it is evident that the FeO -content of the slag plays a decisive role. It is, however, doubtful if any true relationship exists between slag- (FeO) and $[\text{O}]$ in steel, especially during the carbon boil. It is only near the end of refining that $[\text{O}]$ and (FeO) are fairly close to equilibrium, and either of them may be deemed to represent the state of oxidation of the bath. The higher the (FeO) and, therefore, the total iron content (ΣFe) of the slag, the better is dephosphorisation. There is,

however, an optimum (FeO) value (and also an optimum CaO) beyond which no further improvement in phosphorus removal is possible. This is probably because, beyond a certain limit, further enrichment of the slag with iron leads to the formation of calcium ferrite, resulting in an overall decrease of the available lime which offsets the beneficial effect of the (FeO). Further, a large increase of (FeO) decreases the concentration of lime. Again, an excess of lime may result in a part of it remaining undissolved after the saturation limit of the slag for lime is reached.

(d) In order that the phosphorus reaction given by Eq. 8.1 may proceed in the forward direction, it is apparent that the activity of P_2O_5 in the slag should be low, whereas that of CaO, high. The reaction will naturally proceed as long as sufficient lime is available for the formation of $4CaO.P_2O_5$ (or $3CaO.P_2O_5$). This lime would be made available from the amount remaining after the formation of orthosilicate, $2CaO.SiO_2$, with silica. The more the lime available than that corresponding to the tetra-phosphate and orthosilicate, the greater will be the dephosphorisation, and the lower will be the [P]-value reached.

It is evident that a low [P]-content can be attained if the slag- (P_2O_5) is low. For a high-phosphorus burden, this can be achieved by flushing-off the initial slag, which removes the greater part of phosphorus, and making a new one for further removal of the element. In the Thomas process, however, a high- P_2O_5 slag is deliberately aimed at, for such a slag is useful for its conversion into phosphate-fertilisers. In this process also, double slagging is coming into vogue, the first slag being suitable for fertilisers.

(e) Phosphorus can only be removed when the silicon in the metal has attained low values. An excess of base must be present in the slag over that required to form an orthosilicate. The higher the silica content ($M SiO_2$) of the slag, the greater the amount of lime or other bases that is necessary for attaining the desired *V*-or basicity ratio. In the open-hearth, especially, this will result in an unnecessary increase in slag bulk with the consequent low heat transfer from the heating gases to the bath, low productivity, greater loss of iron and manganese in slag etc.

(f) Manganese oxide has usually been regarded as an inert diluent. In fact, it has been shown to affect adversely the dephos-

phosphorability of slags and the dephosphorisation ratio (P_2O_5)/[P] decreases, with increasing MnO, at various (FeO)-contents. It should, however, be remembered that, in steelmaking slags, the components cannot be changed arbitrarily. If the MnO in the slag increases, then for the same FeO, the concentration of CaO has to decrease which should manifest an adverse effect. Schenck and Riess¹ are of the opinion that phosphorus removal is favoured by such an increase because of the formation of manganese silicate, thus giving rise to an excess of free lime. (cf. Fig. 8.1).

(g) The extent of dephosphorisation, expressed by the ratio ($\% P_2O_5$)/ $\% [P]$, depends upon the particular slag and metal compositions. It does not depend upon the amount of the metal or slag. If the slag volume increases resulting in a dilution of P_2O_5 , more of [P] will be oxidised to slag in order to attain the same ratio and thus, lower [P]-values will be attained. The same effect is realised by 'flushing-off' the initial slag, usually at the start of the boil, and its subsequent renewal.

Rephosphorisation ⁴

The factors which are unfavourable for dephosphorisation can cause a rephosphorisation, if they are not under proper control. Thus, a deoxidation in the furnace which lowers the oxygen potential of the bath and the slag may cause a reversion of phosphorus from the slag to metal. However, such a reversion is small, the most important being that during the teeming, when the metal in the ladle reacts with the slag cover. This slag always accompanies the metal during tapping and it is almost impossible to prevent its coming out. The slag cover from the fixed furnaces are quite thick, whereas, from the tilting furnaces, it is much thinner. Since the slag is basic and the ladle refractory material is composed of acidic aluminosilicates, they both react and, thus, there is a considerable silica pick up by the slag (4-5%) which lowers the slag basicity and, therefore, favours a reversion of phosphorus. The factors which increase the fluidity and corrosive action of the slag will, therefore, favour a rephosphorisation. High temperatures increase the lining erosion, increase the slag acidity and, therefore, the rephosphorisation. The same is true for high FeO slags (at constant CaO) because they erode the linings enormously. Therefore, to prevent a phosphorus rever-

sion in the ladle, either the lining must be basic or the steel temperature and (Fe)-slag must be low.

A high Mn-steel favours rephosphorisation because it can also erode the ladle lining. According to Longden,⁵ rephosphorisation is twice as much in silicon killed steels than in the rimming ones. This is partly due to Si in killed steels reacting with slag-(FeO) and being oxidised to SiO₂ and, thereby, decreasing the slag basicity. In the rimming steel, the oxygen potential of the metal is high, which is corroborated by higher Mn-loss in such steels.

Bradaschia⁶ reports of absorption of phosphorus by the basic lining in electric furnaces during the oxidising period and delivering it to the metal during reduction refining. This may happen in the electric furnaces where extensive reducing conditions can be attained. In the open-hearth, such a process is impossible, the conditions being highly oxidising.

Basic Openhearth

It is very useful to know whether the phosphorus reaction attains equilibrium in the steelmaking process. Only when it is known, can measures be taken to influence the reaction one way or the other by varying the compositions of the metal and slag, and the temperature. Schenck and Riess¹ have found that the equilibrium is actually attained, especially at the end of the heats. The [P]-content calculated from the actual slag analysis *cf.* p. 261) and that found from the analysis of the metal were almost similar. Fig. 8.1, showing the influence of the temperature and slag composition on the [P]-content of steel, is useful for the purpose of having a rough estimate of [P] in any particular heat. In Fig. 8.1 (a) and (b), the value $\log K_p - \log (\text{FeO})^5 \cdot (\text{CaO})^4 = \log [\text{P}] / (\sum \text{P}_2\text{O}_5) + 0.06 (\sum \text{P}_2\text{O}_5)$ has been drawn against the temperature for different ($\sum \text{Fe}$), ($\sum \text{SiO}_2$) and ($\sum \text{CaO}$)-contents of slags. From the above equation it follows that, for any given ($\sum \text{P}_2\text{O}_5$) in the slag, the [P]-values can be determined as shown in Fig. 8.1 (c).

Example : A slag containing ($\sum \text{CaO}$) = 44.3, ($\sum \text{SiO}_2$) = 25, ($\sum \text{MnO}$) = 10, ($\sum \text{Fe}$) = 10, ($\sum \text{P}_2\text{O}_5$) = 2.7, is in equilibrium with steel at 1,600°C $\log K_p - \log (\text{FeO})^5 \cdot (\text{CaO})^4 =$

— 1.78. From (c), for the value of —1.78 and $(\Sigma \text{P}_2\text{O}_5) = 2.7$, the phosphorus content of steel is 0.03%.

This figure further shows the favourable effect of increasing (MnO) and of decreasing temperature, especially for slags of low iron contents, on dephosphorisation.

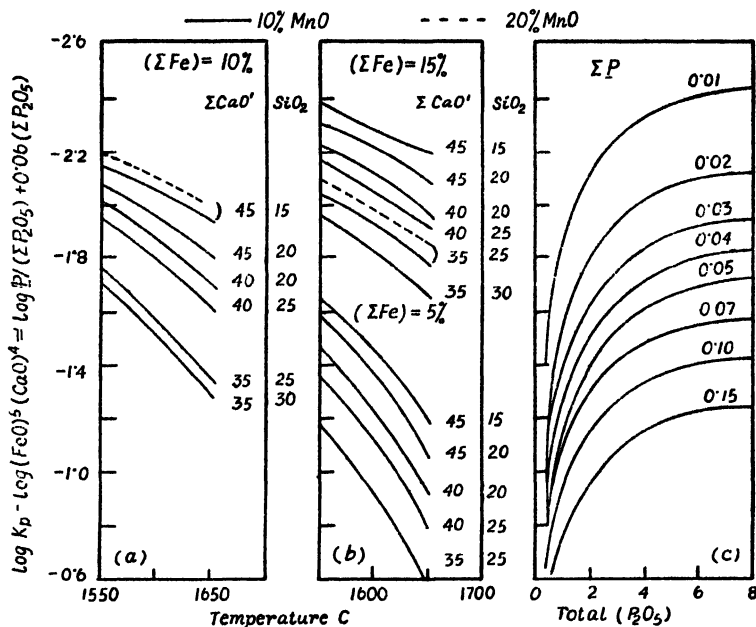


Fig. 8.1—Determination of phosphorus equilibrium in basic steelmaking processes. (By permission from "The Physical Chemistry of Steelmaking" by H. Schenck).

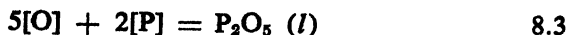
[P denotes phosphorus in steel]

McCance⁷ obtained a linear relationship between CaO-slag and the dephosphorising power given by

$$\frac{1}{[P]} \cdot \frac{(\% \text{P}_2\text{O}_5)}{(\% \text{P}_2\text{O}_5) + (\% \text{FeO})}$$

This has, however, a limited applicability.

The phosphorus equilibrium studies and their applications to steelmaking processes have not given satisfactory results, mainly because of a lack of knowledge of the precise nature of the dephosphorising reaction. Turkdogan and Pearson⁸ suggest a very simplified model for dephosphorisation of iron with molten slags:



They do not visualise the presence of P_2O_5 in the slag as any particular compound and are of the opinion, and rightly so, that it is enough to consider the change in the activity of P_2O_5 during its dissolution in slag. The slag constituents, which combine with P_2O_5 , cause a marked lowering of its activity.

From the values of the equilibrium constant of the above reaction, Pearson⁹ computed the constant of the following reaction :



$$\log K_p = \log \frac{a_{\text{P}_2\text{O}_5}}{(a_{\text{FeO}})^5 \cdot \%[\text{P}]^2} =$$

$$\log \frac{\gamma_{\text{P}_2\text{O}_5} \cdot N_{\text{P}_2\text{O}_5}}{(a_{\text{FeO}})^5 \cdot \%[\text{P}]^2} = 5,250/T - 15.40 \quad 8.5$$

$$\text{where } \gamma_{\text{P}_2\text{O}_5} = \text{antilog } -1.12 (22N_{\text{CaO}} + 15N_{\text{MgO}} + 15N_{\text{MnO}} + 12N_{\text{FeO}} - 2N_{\text{SiO}_2}) - 42,000/T + 23.58. \quad 8.6$$

and the mol fractions of CaO , MgO , MnO , FeO , SiO_2 & P_2O_5 are calculated from the slag composition; the activity of (FeO) can be derived from Fig. 4.4(a).

The phosphorus contents of some basic open-hearth melts have been computed with the help of Eq. 8.5, at various periods before the tap, and the calculated values agree with those determined by analysis. This shows that, under steelmaking conditions, the transfer of phosphorus between the slag and the metal reaches equilibrium fast enough and further, which is important, the attainment of the equilibrium is independent of the carbon content of steel, since the samples taken at various periods contained, naturally, varying amounts of the element.

Pearson⁹ proceeds to suggest another corrected relation for slags containing fluoride. Fluorspar is usually added in the basic open-hearth which improves phosphorus removal. Whether it is caused by an increase in the FeO -activity due to fluorspar or by the lowering of the activity of phosphate ions in the presence of fluoride ions when CaF_2 is added to slags, or due to the slag car-

rying more lime, is not clear. However, in such slags, fluorapatite $3(3\text{CaO} \cdot \text{P}_2\text{O}_5) \cdot \text{CaF}_2$ has always been found and such a compound formation may possibly decrease the activity of the phosphate. Pearson includes the influence of fluoride in the following equation :

$$\log \gamma_{\text{P}_2\text{O}_5} = -1.12 (22N_{\text{CaO}} + 15N_{\text{MgO}} + 15N_{\text{MnO}} + 12N_{\text{FeO}} + 31N_{\text{F}} - 2N_{\text{SiO}_2}) - 42,000/T + 23.58 \quad 8.7$$

The [P]-contents can be calculated by using $\gamma_{\text{P}_2\text{O}_5}$ found from this equation, in the Eq. 8.5.

We may conclude from the above, as well as from the works of Winkler and Chipman¹⁰ that the phosphorus reaction reaches equilibrium in the basic open-hearth reasonably fast, and prior to the end of the heat. Further, the activity of FeO in the slag reasonably depicts the state of oxidation in the slag-metal system, so far as the dephosphorisation reaction is concerned.

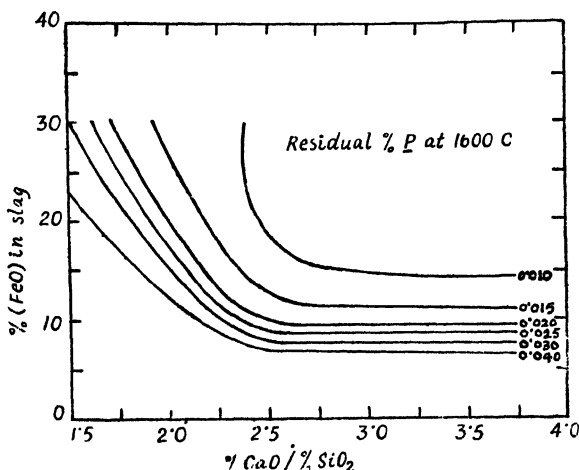


Fig. 8.2—Curves showing the effect of basicity and iron oxide content of slag on residual phosphorus in metal for common basic open-hearth practice. (G. Derge & M. Tenenbaum, Basic Openhearth Steelmaking, AIME, Copyright 1951.)

[P denotes phosphorus in steel]

The equations of Schenck and McCance are relatively cumbersome for use by the melting shop operators. Fig. 8.2¹¹ is very

convenient for the purpose. The basicity of the slag in the figure is a simple $(\% \text{CaO})/(\% \text{SiO}_2)$ ratio and the iron oxide is also in weight per cent. The figure is valid for $1,600^\circ\text{C}$ and for P_2O_5 -contents of 1.5–3.0% in the slag which is the usual range in conventional stationary basic open-hearth practice. The approximate [P]-contents of the metal are shown as series of lines. It can be seen that, in order to obtain minimum [P], the slag must be both highly basic and highly oxidising (*cf.* p. 262). The effect of the temperature is such that the curves move towards higher [P]-contents upwards on the right, with rising temperature.

Practical suggestions

Normally, it is not difficult to obtain a low-phosphorus steel in basic open-hearths if the carbon content of the metal desired is in the lower ranges. This is because a highly oxidising slag can be maintained for the purpose. On the other hand, more care and effort are needed in the case of high or medium-carbon and low-phosphorus steels. In such cases, when the phosphorus content is high, it is sometimes useful to flush-off the initial slag and make a new one (this is usually done in tilting furnaces) but such a recourse would, naturally, delay the process and increase the manganese loss as well as the cost of production. If, however, the SiO_2 -content of the slag is small, it is possible to deal directly with pig-iron with [P] as high as 0.9%.

In the flush-off practice, the initial slag rich in iron is usually drawn out after the melt-down, and in the hot metal-scrap practice, after the addition of molten pig. Because of the prevailing low temperature at this stage (which favours dephosphorisation) and the slag being highly oxidising, a considerable amount of phosphorus is removed, probably as iron phosphate. The new slag made with lime and ore is capable of removing most of the remaining phosphorus and this slag may be kept in the furnace for use, in the next heat, as the initial slag.

As has been already discussed on p. 262, the most important variables for dephosphorisation are the basicity and the iron-oxide of the slag. The viscosity of the slag is also no less important. The basicity ratio CaO/SiO_2 of the slag should be about 2.5–3.0 at the end of refining, with sufficient iron-oxide and fluidity, so that a far-reaching removal of phosphorus is possible.

The high temperature of steel attained in the basic open-hearth before tapping is unfavourable for dephosphorisation. But, on the other hand, such a high temperature is necessary for bringing the lime into solution and obtaining the required basicity. The operator has little freedom to influence the extent of phosphorus removal by varying the temperature. High temperature and high basicity are also essential for sulphur removal.

The phosphorus reaction, as will be discussed on p. 275, is one that takes place between heterogeneous phases (slag-metal) and, therefore, their intimate mixing is of importance. A good 'boil' is a primary requirement for good dephosphorisation. The boil should be controlled in such a way that, at the end of the refining period, the bath oxygen is just enough for the desired product so that the amount of deoxidiser required is not large and, therefore, the danger of reversal of phosphorus to the metal is minimised. Such a reversal is possible by additions like ferro-silicon, which reacts with the iron oxide to form SiO_2 . It reduces the oxygen potential and the basicity of the slag. The dissolution of SiO_2 from the lining of the teeming ladles also reduces the basicity of the slag cover, which induces phosphorus reversion from slag to metal.

In the open-hearth, a low phosphorus metal is obtained in the presence of hot slag rich in lime and iron oxide. Presumably the unfavourable effect of high temperature is offset by the tendency of the hot slag, which probably attains equilibrium with pure lime (i.e., becomes saturated with lime), to absorb oxygen from the heating gases and deliver it to the bath more rapidly than is possible in the case of low-lime cold slags. The rapid delivery of oxygen from slag to bath will raise the oxygen-potential at the metal/slag interface to an optimum and, therefore, lead to a good dephosphorisation, since decarburisation (which reduces the oxygen-potential) takes place, away from the interface, at the hearth. As a consequence, it is evident that a slow rate of decarburisation should improve dephosphorisation, which is a fact.¹² The metal oxygen increases and the phosphorus decreases with an increase in the temperature as well as in the lime – and (FeO)-contents of the slag.¹² Lime, which is of primary importance in phosphorus removal, is regulated by the temperature and the (FeO)-content of the slag.

PNEUMATIC PROCESSES

General

The influence of the various factors on dephosphorisation as enumerated on p. 261, is also valid for the Thomas and other basic pneumatic processes. Before proceeding to consider the effects of these factors, it is desirable to look into the process again in the light of the knowledge gained in the recent years. In brief¹³ as soon as the molten iron comes into contact with the aerial oxygen of the blast, the oxidation of Si and Mn starts and both are reduced to low values in a short time, forming initially an acid manganese silicate. Some carbon is also oxidised away during this period. The acid slag is incapable of retaining phosphorus except in a highly oxidising condition which is however, absent as long as sufficient carbon is present. The oxygen-content of the metal remains below about 0.012%. Due to the non-availability of the exothermic heat of phosphorus oxidation, the prevailing low temperature hinders the dissolution of lime by the acid slag. Lime is only superficially covered with the silicate.

After the completion of the Si and Mn reactions, further blowing eliminates carbon only. During this period, the slag remains acidic, the lime dissolves slowly and the temperature, oxygen-in-steel and oxygen-in-slag rise steadily. At about 0.1% [C], when [O] is between 0.025-0.40%, the phosphorus oxidation becomes perceptible, the temperature rises sharply and the lime starts dissolving rapidly. This phase is the so-called *transition* from decarburisation to dephosphorisation (usually the transition point is taken as the end of the carbon period when [C] \sim 0.02%, which occurs a little later than the sharp temperature increase at [C] \sim 0.1%). The behaviour of oxygen, carbon and phosphorus is shown in Fig. 8.3^{13,14} as functions of oxygen consumed, which is the real variable, rather than as functions of time as is the usual custom.

At the transition, a sufficient build-up of FeO in the slag begins so as to flux the lime which, thereafter, starts dissolving in the slag rapidly and at the end of the process the slag is completely liquefied. At the same time phosphorus oxidation begins in earnest, at a rate increasing tremendously as the blow proceeds, and almost 80% of the total phosphorus is eliminated in the last 3

to 4 minutes. After the transition, the acid slag also changes its character and incorporates sufficient FeO , P_2O_5 , CaO , so as to take the slag composition inside the 'miscibility gap'. The slag 'a' (Fig. 8.4)¹⁴ separates into two layers, in equilibrium, one ($\text{FeO} + \text{MnO}$)-rich but not very basic (point a_1) and the other phosphate-rich (point a_2). As the blow proceeds the slag composition within the gap changes, as shown by the thick line, towards the composition — tricalcium phosphate. The oxygen content of the metal also increases accordingly and at 'point b' it reaches the

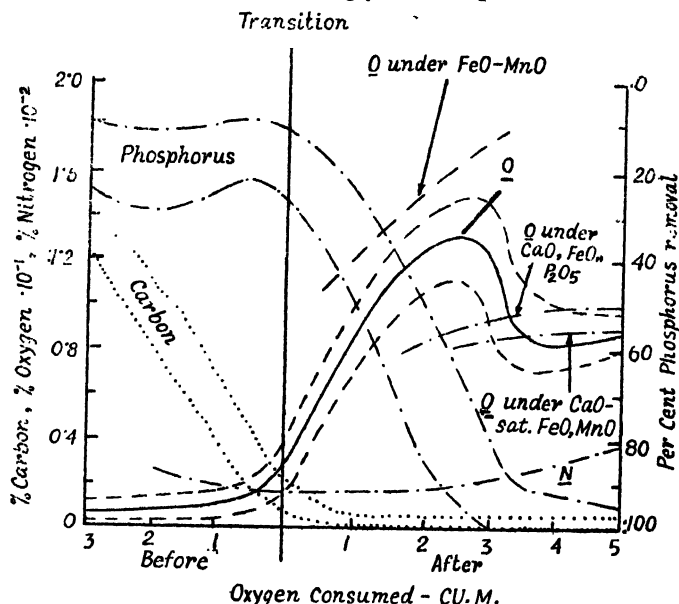


Fig. 8.3—Compositional changes near the end of Thomas process shown as function of volume of oxygen consumed. (By courtesy of Steel & Coal).

[O and N denote their presence in steel]

maximum 0.100–0.145% (cf. Fig. 8.3). The sharp rise in the oxygen after transition must be due to a high FeO -activity of the medium-lime FeO -rich layer. Further blowing takes the composition from 'b', along and inside the miscibility boundary, to the composition 'c' which lies outside the gap and the oxygen-content decreases sharply to 0.070–0.090%. This subsequent fall in the oxygen must be due to the decreased (FeO)-activity of lime-rich homogeneous slag of composition outside the gap. This slag

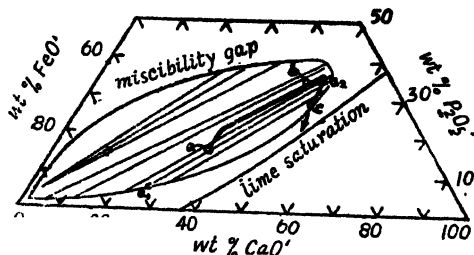


Fig. 8.4—Change of slag composition, shown by bold line, during a Thomas Operation. (W. A. Fischer & H. Straube, *Stahl und Eisen*, 80, 1960, 1202). Lime saturation line is also shown.

determines the ultimate oxygen-content of the low-carbon conventional Thomas steel. The fall in the oxygen-content is directly connected with the manganese 'hump'. The Mn-reversion occurs because of deoxidation by the phosphorus, which itself is oxidised at a very fast rate.

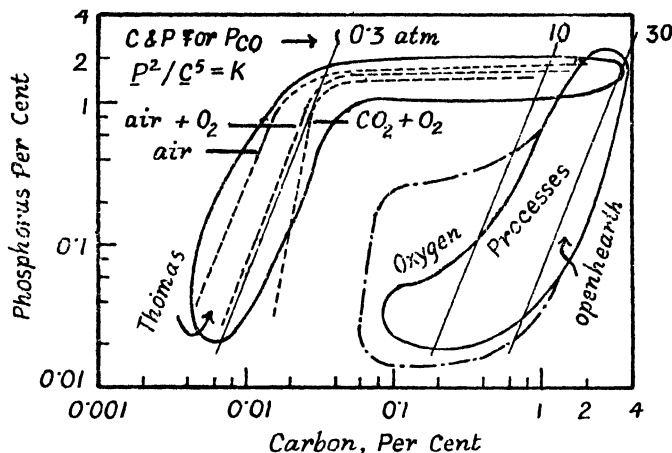


Fig. 8.5—Relation between carbon and phosphorus removal in the basic open-hearth, top blown oxygen and Thomas processes. (....experimental results of Pottgiesser).

Fischer and Straube¹⁴ find that the transition invariably occurs at oxygen 0.027–0.038% in the metal, the average being 0.034%. This critical value is a primary condition for rapid dephosphorisation. Although the presence of an oxidising liquid basic slag is essential to bind phosphorus and retain it, it is certainly not the only major factor for the start and continuation of dephosphori-

sation. The critical oxygen content is another factor without which the rapid phosphorus removal cannot occur. How the critical value is obtained, even in the presence of high carbon contents, in cases where dephosphorisation precedes decarburisation, is a matter of great interest and importance and is discussed later.

The picture now becomes simple. The phosphorus elimination starts slowly, while there is still some carbon ($\sim 0.1\%$) in the metal, by an iron-rich slag of medium basicity. The initial high and rising oxygen in the converter metal is determined by the high (FeO)-activity of the (FeO+MnO)-rich layer of the slag, containing impurities of CaO and P_2O_5 which separates out from the initial acid silicate. After the oxygen has reached the maximum (and during the period lime has been dissolving slowly), the dissolution of lime becomes extremely rapid and the major portion of phosphorus is removed in a short time by a lime-rich slag with medium (FeO)-activity. The slag, later, leaves the gap and becomes homogeneous, with the consequent decrease in the (FeO)-activity which lowers the metal oxygen. At the end of the process, the oxygen content is largely determined by the slag, since it is nearly in equilibrium with the metal so far as oxygen is concerned.

Now, why does phosphorus removal in the Thomas process start after most of the carbon has been eliminated, whereas the reverse is possible in the open-hearth (or other basic oxygen processes)? In both the processes, if the simultaneous oxidation and removal of the two elements are followed, it is found (cf. Fig. 8.5^{12,15,16}) that the slopes of dephosphorisation in the both are similar. Carbon and phosphorus burn off in the ratio of 5 : 2 giving a relationship, $P^2/C^5 = \text{constant}$. Fig. 8.5 also shows that the CO in the open-hearth evolves at about 100 times higher pressure than in the Thomas process, i.e. at ~ 30 atm., as compared to $p_{CO} = 0.35$ atm. in the latter process. Since carbon and phosphorus are removed by oxidation, it is evident that they can only be related through the oxygen-content of the metal. This means that, for the same [C]-and [P]-contents, the open-hearth metal should be 100 times richer in oxygen than the Thomas metal, i.e. dephosphorisation in the former should take place at 100 times higher [O]-concentrations than in the latter.

Such a build-up of oxygen or CO-pressure in the open-hearth is, however, contrary to findings, although it is a fact that there as well as, to a lesser extent, in the Thomas process, the metal is more oxidised than the carbon content would indicate. Carbon is a good reducing agent and does not allow [O]-concentrations to increase greatly as long as any nucleation and CO-evolution in the liquid metal can occur (Thomas process). Where there is a lack of such facilities (as in the open-hearth, top-blown oxygen processes, etc.), carbon behaves as an unsatisfactory reducing medium and an [O] build-up in the metal is possible which far exceeds the [C]-[O] equilibrium value. Such a local build-up in the metal, especially at and near the slag/metal interface, in the presence of basic oxidising liquid slags leads to dephosphorisation when [O] exceeds 0.025-0.04%. Such a thing is possible in the open-hearth even when a large amount of [C] is present because the carbon reaction takes place at the hearth, away from the said interface. In the Thomas process such a condition occurs when carbon sinks below about 0.1%. It is a fact that the phosphorus reaction in the open-hearth reaches equilibrium with the slag, independent of the [C]-content. One must, therefore, conclude that the phosphorus reaction takes place at the metal/slag interface and depends upon the delivery of oxygen from the slag and phosphorus from the metal to the interface. In the open-hearth, the supplies are maintained by the turbulence caused by the boil. A thorough intermixing of slag and metal is an important pre-requisite for a good dephosphorisation or for that matter, any interfacial reaction.

In short, as long as the carbon reaction proceeds freely, the oxygen level is not sufficient to effect a dephosphorisation. A build-up of oxygen in the metal is possible if the carbon reaction is suppressed for lack of nucleation. Phosphorus elimination depends not only upon the availability of the needed oxygen but also on the presence of a liquid basic slag. Thus, although both the elements are eliminated *via* oxygen, their zones of reaction are different. This zonal separation of the carbon and phosphorus reactions has been the basis of the newer developments in oxygen steelmaking processes.

The increasing demand on low-nitrogen steels has led to the use of pure oxygen as a refining medium in the so-called LD- or

top-blown converters. Newer and modified processes have been developed, mainly for using high-phosphorus iron akin to Thomas pig. In the top-blown process, the high pressure oxygen jet which impinges on the metal surface creates a shallow depression. The blast does not enter the bath deeply but is reflected back, together with droplets of iron, upwards and outwards. Around the area of impingement, a temperature zone of $2,500^{\circ}$ - $3,000^{\circ}\text{C}$ is formed. These droplets become immediately oxidised and flux some of the lime, which is liquefied at that high temperature. This highly oxidising and low-basic liquid slag is capable of phosphorus removal, provided there is a thorough intermixing between metal and slag.

The most striking difference between the top- and bottom-blown pneumatic processes is that, in the former, dephosphorisation precedes or proceeds simultaneously with decarburisation, whereas in the latter the phosphorus removal is delayed until almost the entire carbon is eliminated. In the Thomas process, because of the facility of nucleation afforded by the aerial nitrogen bubbles, the carbon reaction proceeds fast and its reducing action keeps the metal oxygen to a low level. This factor together with the little basic still-hot-liquid slag prevents a dephosphorisation until the carbon level sinks to a low value, although the metal and the slag are intermixed thoroughly by the blast.

In the top-blown process, the oxygen supplied to the system mostly accumulates in the slag as iron oxides and only a little in the metal at the beginning, when the carbon reaction is absent. This slag delivers the oxygen to the bath as in the open-hearth, except the portion directly supplied to the whipped-up iron droplets. Silicon and manganese in the metal are oxidised by the diffusing oxygen (or when in contact with the slag). They do not, however, require the presence of a slag for their oxidation as in the case with phosphorus. The carbon oxidation takes place wherever there are gas pockets to facilitate nucleation. But, for phosphorus removal, its migration to the slag/metal interface is necessary, which depends upon the convection inside the bath and physical intermixing between the metal and the slag. The carbon boil determines the convection current. But the physical intermixing can only be effected by the air blast as in the Thomas process or by rotating the converter vessels as in the Kaldor or in the

elliptical processes or by secondary bottom-blowing in the top-blown converters. Thus, phosphorus removal in the LD can be accelerated or intensified by a mild turbulence introduced by blowing air through the bottom. An excessive turbulence will create conditions similar to that in the Thomas process; decarburisation will be rapid and may precede dephosphorisation and ultimately an after-blow as in the Thomas process will be necessary. These processes effect a faster rate of decarburisation than in the stationary LD-converter and therefore the iron-oxide build-up in the slag is less. But dephosphorisation, even with a less oxidising slag, is extensive since the turbulence causes a faster transport of the phosphorus atoms to the place of reaction. In the rotating processes, a high (Fe)-slag and, therefore, a good dephosphorisation can be achieved at a slow rotating speed; subsequently, in order to lessen the iron loss, the speed can be increased to effect a high decarburisation rate, with the consequent low (Fe)-slag.

In the Thomas process, dephosphorisation depends upon the extent of slag/metal interface and therefore broken lime is more active and liquefied earlier than lump lime.¹⁷ Also, the influence of silica is greater because the high melting orthosilicate of lime covers the active surface of the base. In the top-blown process, phosphorus removal depends more upon the rate of transport of the element to the base and, therefore, upon the convection in the metal, rather than on the size of lime or amount of silica.¹⁸

A comparison of the rotating cylindrical and elliptical vessels, in respect to the phosphorus reaction, clearly brings out its intimate relation with the carbon reaction, (Fe)-slag, [O]-metal, turbulence and intermixing of slag and metal.¹⁹ In an elliptical vessel (axes ratio $a/b = 1.5$), the greatest dephosphorisation rate is found between 14-16 r.p.m. At lower r.p.m., the rate is low although the (Fe)-slag is high and decarburisation slow. This is because of an insufficient intermixing, which causes a slower delivery of oxygen from slag to metal and reduces the slag/metal interfacial area. Above 16 r.p.m., the oxygen delivery and intermixing are so high that the carbon reaction is greatly accelerated which reduces the (Fe) and [O] and inhibits phosphorus oxidation. The increase and the decrease of dephosphorisation with r.p.m. are shown in Fig. 8.6(a). Since the rate is

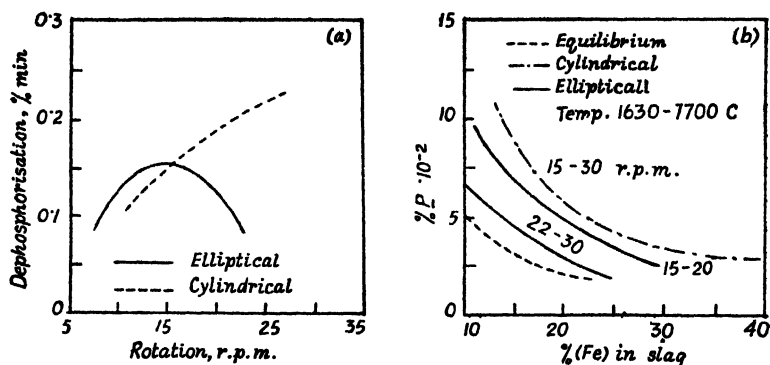


Fig. 8.6—Relation between (a) rates of rotation & dephosphorisation and (b) phosphorus in metal & iron in slag for different rotation rates, in cylindrical and elliptical vessels. (P. E. Hardt, G. Vocke & H. Schenck, *Stahl und Eisen*, 81, 1961, 155-63.)

highest at 14-16 r.p.m. in the presence of an iron-rich reactive basic slag, the metal possesses the highest oxygen at that revolution, which effects a dephosphorisation at high [C]-contents.

In a cylindrical vessel, the decarburisation rate does not increase correspondingly at high r.p.m., after the initial steep rise, as happens in the elliptical vessels (see p. 218). Therefore, it is natural that in the cylindrical types, the dephosphorisation rate should not decrease with increased r.p.m. This is shown in Fig. 8.6(a) where dephosphorisation increases as the r.p.m. increases (simultaneously with the increase in decarburisation). The strengthened CO-evolution helps to create an increased turbulence which, in its turn, helps phosphorus transport to the places of reaction but the turbulence is not enough to accelerate the C-O reaction to a height as to precede phosphorus removal.

The above considerations throw a light on the kinetics of phosphorus reaction in the steelmaking processes. The phosphorus reaction does not reach an equilibrium even with all the turbulence and intermixing in the Thomas process. It is to be expected that, in other pneumatic processes, the reaction would be away from the equilibrium. In fact it is so. But the equilibrium may be approached if a sufficient turbulence can be created. Fig. 8.6(b) shows the increasing nearness of phosphorus to the equilibrium values of Fischer and Vom Ende²⁶ as the speed of rotation increases in the elliptical vessel. In the stationary LD-

vessels, the same purpose can be achieved if, simultaneously with the top-blowing, a mild bottom blow with oxygen/air ratio of 6 : 1 is effected.³³ In the Thomas metal, [P] can be brought down by creating an artificial turbulence with the CO evolved on adding about 5-10 Kg. of Stahleisen (open-hearth pig) per ton. The CO creates a stir which enables a further reaction between metal and slag.³⁴ In the PL-process,³⁵ after the oxygen-blow on steel in the tilted converter, the vessel is again raised vertically and further blown with air. This consequent intermixing between metal and slag brings [P] down to the level found in the Thomas process (cf. Fig. 8.14).

The difference in the relation between the rates of decarburisation and dephosphorisation in the Rotor and top-blown converters and in the Thomas process (using air or oxygen-enriched air) is clearly shown in Fig. 8.15.

Foaming of slag^{13, 20}

During the oxygen blow, foam has been observed to form in the slag. It is said that such foaming is a necessity. But it is rather an indication of the proper state of oxidation of the slag and of agitation of the bath (for diffusion of phosphorus to the slag/metal interface). Foaming is caused by carbon-containing iron droplets, whipped off the bath and held in the slag, whose oxygen reacts with the carbon and forms CO gas. This inflates the slag. If the state of slag oxidation is not adequate, carbon will not be oxidised to any extent and foaming is inhibited. This happens when the oxygen jet is too penetrating and the slag is not properly oxidised. If the jet strikes the slag only superficially, foam will no doubt form but the carbon and phosphorus eliminations will be considerably delayed. Only a controlled foaming will lead to a successful operation.

Summary

The above discussions show that, for a proper control of the oxygen-lancing processes in stationary converters, what is necessary is a highly oxidising liquid basic slag and a sufficient, but not too much, stirring of the bath. This has led to the trial of rotating furnaces, using oxygen-jets on the slag, which serve both the above purposes. A proper control of the speed of rotation would

enable variations in the degree of stirring and the rate of decarburisation. While the Kaldor and Rotor processes have passed the experimental stage, the elliptical vessel is still under trial.

In the bottom-blown converter, the blast causes widespread agitation and provides nuclei for the CO-evolution so that the bath is not oxidised enough for the purpose of dephosphorisation, till most of the carbon is eliminated.

The open-hearth refining is characterised by the fact that while all other reactions occur at the slag/metal interface, decarburisation occurs at the hearth bottom because of difficulties of nucleation at other locations. The velocities of all other reactions are, however, dependant upon the agitation caused by the carbon boil.

Thomas Process

The influence of the various factors on phosphorus removal has been discussed on p. 261. We will now consider them from the point of view of actual Thomas steelmaking.

Effect of slag FeO and CaO : The most important variables that affect dephosphorisation in the Thomas process are the lime- and iron oxide-contents or their activities in the slag. Both favour phosphorus removal. This aspect has been discussed elaborately on pp. 100-03 from the point of view of a pure $\text{CaO-FeO-P}_2\text{O}_5$ slag. How the common impurities in the Thomas slag affect the phosphorus reaction will be seen later. We have seen that it should be the endeavour of Thomas blowers to obtain a slag at the end of the process whose composition lies in the narrow corridor between the lime-saturation line and the miscibility boundary (cf. Fig. 3.26). Therefore, the addition of lime to the charge before blowing is so adjusted, taking into consideration the Si-, P-, Mn-contents of pig-iron and the silica-content of ore additions, that the final slag composition lies within this narrow region. Too much of lime will not be helpful, since its solubility is limited by the saturation-line and the excess will remain undissolved and unable to take part in the slag/metal reactions. Lime-saturation, however, exhibits a maximum dephosphorising power.

We have seen, in Fig. 8.4, the movement of the slag composition during a Thomas blow. The nearness of the composition to the lime-saturation line or the miscibility boundary is determined by the CaO- and P_2O_5 -contents of the slag. As the blow pro-

ceeds, if the composition moves from the lime-saturation towards the gap boundary in the direction of higher P_2O_5 and lower CaO and FeO in the ternary diagram, the $[P]$ -content increases rapidly; while, if it moves towards higher P_2O_5 and FeO and lower CaO , the $[P]$ -content may increase slightly or even remain almost the same. This is because the deleterious effect of the decreasing lime activity is adequately compensated by the increasing (FeO) -activity.

In the presence of an excess lime, the initial slag after the transition approaches the lime-saturation line and moves along it. Along this line, the metal should contain lowest $[P]$ -contents, as given by equilibrium experiments. As more and more of iron is oxidised, the composition leaves this line and moves towards the miscibility-gap. The $[P]$ -contents should slowly increase. If an excess of lime is absent, the slag composition from the beginning will not approach the saturation line and would rather move, from outside, along the miscibility boundary. This certainly would not lead to as low $[P]$ -contents as is possible with excess lime. If the metal is over-blown to an extent that the iron oxide increases greatly and the slag enters the gap, a rephosphorisation is to be expected. (cf. p. 103).

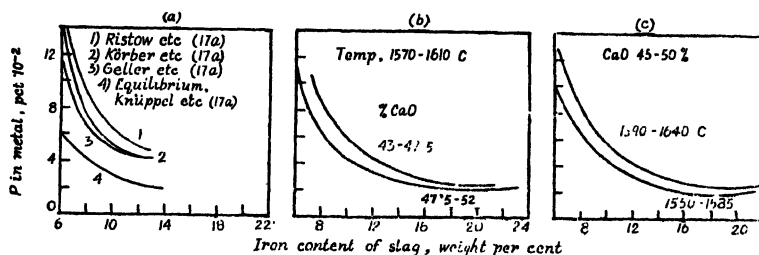


Fig. 8.7—Relation between phosphorus in metal & iron in slag. (b) & (c) show the relations for different groups of temperatures and lime contents of slag.

It has been customary to correlate P -metal and (Fe) -slag and curves, hyperbolic in nature (Fig. 8.7(a)), have been obtained. This shows that $[P]$ -decreases with increasing (Fe) . The curves, no doubt similar in trend, show considerable variations, which can only be attributed to the variations of lime and the temperature not having been taken into account. Both these factors affect dephosphorisation to a great extent. Figs.¹⁷ 8.7(b) and (c)

show the relation $[P]$ and (Fe) , for two different groups of temperatures and lime contents of the slag. It is clear that higher lime leads to lower $[P]$, for the same (Fe) and temperature; and for the same lime and temperature groups, higher (Fe) leads to lower $[P]$. The dephosphorising power of (Fe) , it seems, decreases with increasing (Fe) and over about 20% (Fe) , the $[P]$ reaches a minimum and remains almost constant or rather, the curves bend upwards showing a possibility of rephosphorisation. The lower the (Fe) the higher must be the lime and lower the temperature in order to reach the lowest possible $[P]$ under any given conditions. For normal Thomas slags, with 10-12% (Fe) , the $[P]$ usually reached is about 0.04%.

Lime effects a better dephosphorisation at higher temperatures and the effect is more, the lower the (Fe) . This can be seen in Fig. 8.8¹⁷, where curves of $[P]$ and CaO are drawn for two groups of temperatures and iron-contents of the slag. Fig. 8.8 shows clearly that, for low- (Fe) slags, the basicity ratio has a profound influence on $[P]$. Slags containing more than 20% (Fe) show a flatter run than with lower (Fe) . It is to be noted that above 50% CaO , instead of a better dephosphorisation, there is rather a worsening effect.

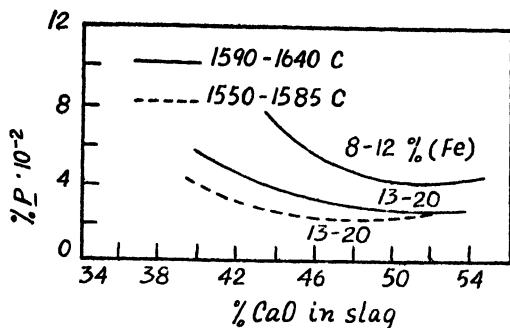


Fig. 8.8—Influence of the slag-lime on the P-content of metal for different groups of iron contents of slag & temperatures. (F. Weber & Th. Kootz, *Stahl und Eisen*, 78, 1958, 1736).

[P denotes phosphorus in steel]

The size of the charged lime has some effect on phosphorus removal. Small-sized, graded lime pieces lead to lower $[P]$ -contents, especially if the iron-content of the slag is on the low side.

The beneficial effect of fine lime is perhaps due to its more rapid dissolution in the slag.

Effect of temperature : Because of the exothermic nature of the phosphorus removal reaction, it is understandable that lower temperatures lead to better dephosphorisation, as seen in Fig. 8.8. The beneficial effect is smaller if the process is carried out with high iron- and lime-contents in the slag. It has been found that $[P]$ is about double the value given by Trömel and Oelsen in their equilibrium experiments with lime-saturated slag at high temperatures. $[P]$ approaches the equilibrium value only at low temperatures $\sim 1,550^{\circ}\text{C}$.

The strong influence²¹ of the temperature can be easily understood from its effect on the miscibility gap and the lime-saturation line. As the temperature decreases, the saturation line moves towards the gap boundary because the lime solubility decreases; and the immiscibility increases, resulting in an enlargement of the gap. The activities of both the lime and the (FeO) would, therefore, naturally increase in the narrow region between the 'gap' and lime-saturation boundaries and such an increase in their activities would result in a better phosphorus removal.

Effect of SiO_2 : Normally, one would assume that SiO_2 in the Thomas slag would retard phosphorus removal, since it reduces

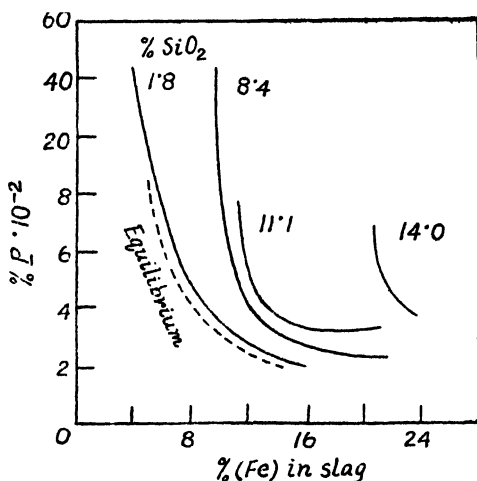


Fig. 8.9—Influence of silica on phosphorus content of metal (Th. Kootz & H. J. Uberhorst, *Stahl und Eisen*, 81, 1961, 241)

the slag basicity. In the laboratory experiments, however, it has been ascertained that, within limits, SiO_2 does not adversely affect $[\text{P}]$ as long as the slag remains saturated with lime.²² Weber and Kootz,¹⁷ in their converter experiments, also found no unfavourable influence on $[\text{P}]$ with slags containing 4.5% and 6.2% SiO_2 .

However, there is considerable evidence to the contrary.^{23,24} Kootz and Uberhorst²³ related $[\text{P}]$ with (Fe) as shown in Fig. 8.9. The detrimental influence of SiO_2 is clear. The higher the SiO_2 , the greater is the end-phosphorus, for the same (Fe) -slag. With SiO_2 -poor slags, dephosphorisation can be assumed to set in early, i.e. at low (Fe) -contents. In other words, the lime is liquefied and becomes reactive at low (Fe) and soon after the transition. As the silica-content increases, the liquefaction of the slag and the onset of phosphorus removal are delayed and occur at higher (Fe) and the end- $[\text{P}]$ is also higher.

An increasing silica content naturally decreases the lime activity. Simultaneously, the (FeO) -activity is also lowered. For the same a_{FeO} , the $[\text{P}]$ -content is somewhat lower in case of low-silica slags. The diminution of the activities of both CaO and FeO affects phosphorus removal. Dephosphorisation starts only in the presence of a liquid basic reactive slag. With an increasing silica, more of viscous calcium orthosilicate is formed which needs to be fluxed by FeO . The change from the initial $\text{FeO-SiO}_2\text{-CaO}$ system to the $\text{FeO-CaO-P}_2\text{O}_5$ system is delayed. Therefore, the phosphorus removal is also suppressed and delayed.

It may happen that, sometimes, the $[\text{P}]$ decreases with decrease in FeO -activity.²⁴ But, in the steelmaking slags, any one component is related to others and cannot be varied independently without affecting them. Thus, as the FeO decreases, the lime content of the slag increases and approaches the lime-saturation line, resulting in an increase in its activity. The beneficial effect of the increased lime-activity more than offsets the adverse effect of decreased FeO , which leads to overall lower $[\text{P}]$ -contents.

Effect of P_2O_5 : We have seen in Fig. 8.7, the close interrelation between (Fe) and $[\text{P}]$. But, as shown by Speith *et al*²⁵ there is a similar connection in the Thomas slag between (Fe) and (P_2O_5) ; the latter decreases as (Fe) increases. Therefore, there

must be a close relation between (P_2O_5) and $[P]$; and the ratio $(P_2O_5)/[P]$ may be studied as a function of either (P_2O_5) or (Fe) .

The ratio $(P)/[P]$ is drawn in Fig. 8.10²⁵ against both (P_2O_5)

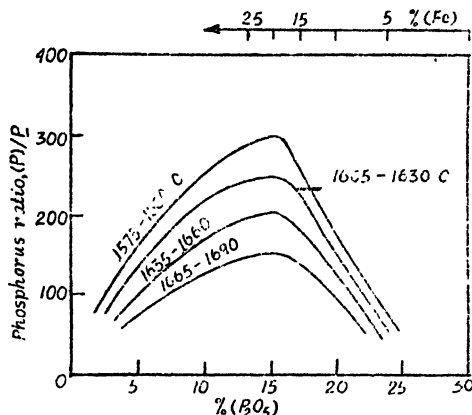


Fig. 8.10—Phosphorus distribution between slag and metal in the Thomas process as function of (Fe) and (P_2O_5) in slag. (K. G. Speith, H. v. Ende & G. Mahn, *Stahl und Eisen*, 80, 1960, 1763.)

and (Fe) , for four different groups of temperatures. The curves show average values obtained from the Thomas works data. The maximum ratio is given with (Fe) between 15-20%. The ratio decreases with an increasing (Fe) and a decreasing (P_2O_5) . As (Fe) increases, the a_{FeO} also increases; but beyond about 15-20% (Fe) , the activity remains more or less constant even with an increasing iron content. Thus, beyond ~20% (Fe) , at constant a_{FeO} the phosphorus ratio decreases with P_2O_5 . Since, as can be gathered from Fig. 8.10, the P_2O_5 -content decreases more rapidly than $(P)/[P]$, it is evident that the $[P]$ -content would simultaneously decrease. The $[P]$ -content does decrease with (P_2O_5) and the fall is steep below about 15% P_2O_5 .

As the a_{FeO} does not increase after the (Fe) -content has reached 15-20%, it would be futile to further increase the iron-oxidation for attaining low-phosphorus steels. A very low phosphorus steel can be made by decreasing the (P_2O_5) without increasing the (Fe) beyond 15-20%. It should be borne in mind here that the lime plays a decisive role in dephosphorisation. The P_2O_5 must combine entirely with lime to form a stable phosphate. With a given (Fe) -content, the lower the P_2O_5 in a Thomas slag,

the more the lime at its disposal for binding P_2O_5 . Since $[P]$ is closely connected with the CaO/P_2O_5 ratio and the higher the ratio the lower the $[P]$, it is clear that the more the excess lime, the lower will be the $[P]$.

Although a low P_2O_5 in the Thomas slag may produce a low $[P]$ -steel, the process itself will be uneconomical, since the slag with P_2O_5 lower than 16-17% will not be saleable at a profit for the purpose of making fertilisers. Too much of iron also deteriorates the citric acid solubility of the slag. To reach low $[P]$, the only way is to drain off the first slag and make a new one with the addition of lime and re-blow for 20-40 secs. A $[P]$ -content of 0.01-0.02% can be reached with a slag containing about 10% P_2O_5 and (Fe) less than given by the (Fe)- $[P]$ relations. The process is known in Germany as 'fine-dephosphorisation'. (cf. p. 288).

Effect of $[Mn]$ and (MnO) : There have been different opinions regarding the effect of manganese on the phosphorus content of metal. The calculations of K_{Mn} from the metal and slag analysis show values comparable with those obtained from the equilibrium with pure FeO-MnO slag. Since (FeO) or (Fe) is directly related to $[Mn]$ and to $[P]$ as well, it is natural that $[Mn]$ and $[P]$ should also be inter-related. The calculated relation between them, for different temperatures, is shown in Fig. 8.11.²⁹ Kosmider and Schenck²⁹ have shown that the results from the Thomas works data follow the curves precisely. It is to be noted that, in contrast to the basic open-hearth, a low $[P]$

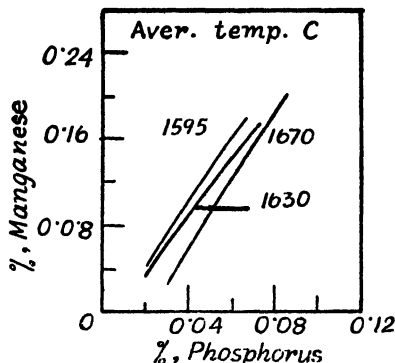


Fig. 8.11—Relation between the Mn- and P-contents of the metal at different temperatures. (H. Kosmider & H. Schenck, *Stahl und Eisen*, 74, 1954, 1291.)

indicates a low $[Mn]$ and a high (MnO) in the slag. Also, for a given $[P]$, the $[Mn]$ -content is lower the higher the temperature. Therefore, it is uneconomical, in view of the manganese oxidation losses, to strive to obtain a low $[P]$ when the metal temperature is high.

However, Kootz *et al* ²³ could not find any influence of manganese on dephosphorisation. According to them, phosphorus removal sets in, irrespective of the MnO -content of the slag, at the same stage depending upon the lime-liquefaction and the iron-content of the slag. The $[P]$ -content is also not affected by high or low manganese in the slag.

Effect of alumina: Generally, the alumina content of the Thomas slag remains below about 1%. At higher concentra-

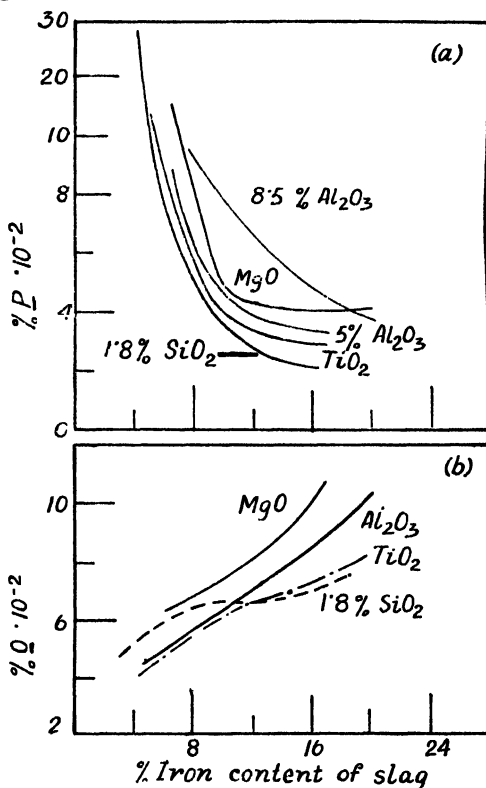


Fig. 8.12—Influence of magnesia, alumina & titania on dephosphorisation and oxygen content of metal. (Th. Kootz & H. J. Ueberhorst, 81, 1961, 244).

tions, the slag liquefaction and dephosphorisation start much earlier. The rate of the latter becomes somewhat slower later and the end-[P]-content higher than usual (*cf.* Fig. 8.12a)²³. This finds confirmation in the lower [O] at low Fe-contents and higher values later (Fig. 8.12b)²³ when the reducing action of phosphorus is no longer so strong.

Effect of TiO_2 : The liquefaction of the slag and the start of dephosphorisation are earlier for TiO_2 contents of 1.5-6.5% in the slag. However, the [P]-content approaches the values of TiO_2 -free blows (*cf.* Fig. 8.12a). The oxygen-content is at first lower but then later follows that of the TiO_2 -free blows (*cf.* Fig. 8.12b).

Effect of MgO : Magnesia is soluble in Thomas slags, with 16-20% (Fe), to the extent of 4-6%. In its presence, dephosphorisation starts a little later and ends at higher [P] than usual (*cf.* Fig. 8.12a). The oxygen values are also higher as in the above cases (*cf.* Fig. 8.12b). This is understandable since CaO and MgO both reduce each others solubility in the slag.

Magnesia enters the slag from the dolomite lining and the fluxing action increases with temperature³⁶. Thus, the stronger adverse influence of the high temperature on dephosphorisation in works practice, in comparison with the laboratory experiments with MgO-free slags, may be due to the fluxing of more of MgO.

Effect of CaF_2 : Fluor-spar fluxes the lime and starts dephosphorisation early. Because of the reducing action of phosphorus, the oxygen initially is low but later rises and both [P] and [O] assume normal values, with increasing (Fe)-content of the slag. Because of an early start of dephosphorisation, i.e. at higher [C] and lower [O], the end [C]-content is higher than usual.

Fine Dephosphorisation ^{18, 28, 30-32}

The phosphorus content reached in the normal Thomas process is about 0.04-0.05%. In view of the fact that low-nitrogen steels can be made easily in the Thomas converter (*cf.* p. 30), it is necessary to attain a low phosphorus as well, so that the Thomas steels may be comparable to high quality open-hearth ones. In the open-hearth, it is not difficult, when using a low-phosphorus charge, to attain 0.008-0.020% [P]. In the Thomas

process, such low values can be obtained, if at all, by increasing the iron-content of the slag considerably. A high iron, however, makes the slag unsuitable for the purpose of fertilisers and, therefore, makes the process uneconomical. It is, therefore, necessary to carry out the process in two stages.

The two stage process has both economic and technical advantages. At first, the normal blow is continued upto about 0.06-0.10% [P]. The slag formed is suitable for making fertilisers since it contains high P_2O_5 and low-iron. It is not blown to lower [P] since the blower cannot visually estimate the phosphorus-content correctly from steel samples below $\sim 0.06\%$ [P]. At this stage, the blow is stopped, the converter tilted and the initial slag drained off as far as possible ($\sim 50-70\%$). Then, the additions like lump or powdered lime, graded lime-stone, soda or mill-scale, either singly or all together are made to form the second slag and blown for 10-60 sec, depending upon the temperature and the [P] attained in the first stage. Blowing can also be done only with the slag remaining after the drain-off.

The additions for making the second slag are not at all necessary and they only disturb the continuity of the process. Blowing with the remaining or 'rest' slag does produce very low-phosphorus steel. Although the second slag contains a high percentage of (Fe), the overall loss of iron in the slag is not such as to make it uneconomical because the quantity of this slag is small.

The basicity and lime-content of the slag in fine-dephosphorisation assume great importance. De- or re-phosphorisation depends upon whether the slag composition lies outside or inside the miscibility gap. Therefore, the quantity of the lime has to be calculated on the basis of the phosphorus- and silicon-contents of the charge so that, at the end, the composition lies outside the gap. In the case of fine-dephosphorisation, a greater care must be taken in the calculations since the iron-content of the slag becomes very high and there is every danger of a rephosphorisation. The lime-unsaturated slags lying in the region between the saturation and the gap possess great dephosphorising power.³⁷ This power increases as the lime composition approaches saturation and lowest [P]-values can be attained when the slag becomes saturated with lime.

In order to maintain the same slag composition, as far as possible, in case of differing P and Si in pig-iron, Kosmider and Schenck²⁸ propose a table for the quantity of lime to be used for different P- and Si-contents, taking into consideration the formation of triphosphate and orthosilicate and keeping an excess of about 70%. They show the [P]-content reached as a function of (Fe)-slag for high and low lime additions, e.g. 140 Kg and 115 Kg of lime/t pig-iron. A low [P] \sim 0.022% is reached with the higher lime. This is valid irrespective of whether one slag or two slag processes have been used.

LD Process ^{13, 38-43}

The conventional LD-process with low-phosphorus pig is metallurgically similar to the open-hearth. The use of oxygen lancing enables an early formation of high (Fe)- and low-basic slag which is capable of phosphorus removal. Although the (Fe)-content decreases as more and more of lime dissolves and dilutes the slag, the (FeO)-activity remains somewhat uniform since, for any given (Fe), the oxide-activity increases as the basicity increases (cf.

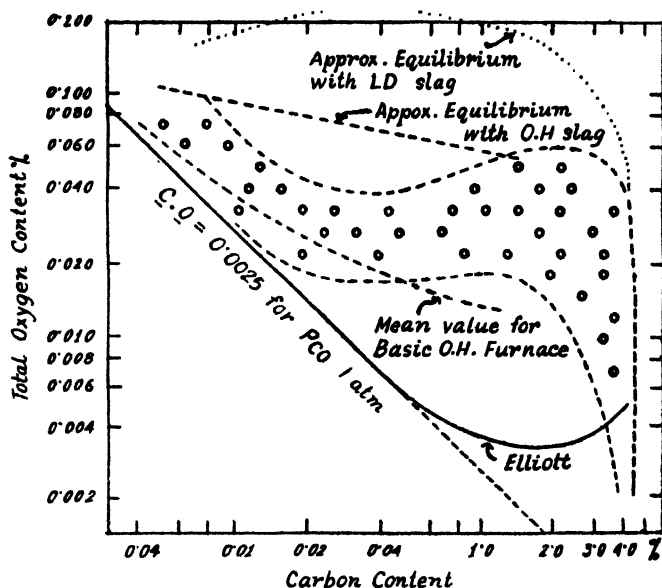


Fig. 8.13—Carbon & oxygen contents in LD & open-hearth processes and oxidising power of corresponding slags. (By courtesy of Steel & Coal).

Fig. 4.5). Thus, a decrease in (Fe) is compensated by an increase in lime, so far as the (FeO)-activity of the slag on the acid side is concerned. Such an increasingly basic and highly oxidising slag is very suited for dephosphorisation.

The oxygen content of LD steel during the blow is much higher than in the open-hearth (*cf.* Fig. 8.13^{13, 38}) which means the metal is more oxidised, i.e. the retardation of the 'boil' is more effective than in the open-hearth. Dephosphorisation can begin very early, even at 3% [C], since at this value the critical oxygen content 0.025-0.040%, essential for phosphorus removal, is exceeded. This high oxygen, the sluggish carbon boil and the highly basic and oxidising slag cause extensive dephosphorisation which also precedes carbon elimination.

Phosphorus elimination is not difficult, as shown in Fig. 2.6, and its content upto 0.5% can be worked by merely adding more lime. Its removal can be made to precede that of carbon, without any substantial increase in the blowing time, by lowering the oxygen pressure and raising the lance. In fact, the decarburisation rate can be varied at will by increasing or decreasing the distance of the lance nozzle from the metal surface and varying the amount of oxygen per min. The rate and extent of dephosphorisation can be varied by additions of ore and/or scrap as coolants. Ore is also useful for the supply of oxygen, the liquefaction of lime as well as for increasing the (Fe)-slag.

Using \sim 9% lime and \sim 4% limestone, a pig with P \sim 0.5%

Pig iron			Steel		
Si	Mn	P	Si	Mn	P
1.22	2.02	0.35	0.06	0.27	0.018
1.03	2.15	0.43	0.13	0.36	0.022

Slag						
Fe	P ₂ O ₅	CaO	SiO ₂	Al ₂ O ₃	MgO	Mn
14.40	3.15	49.80	11.42	2.74	4.16	7.25
17.50	4.25	37.70	14.30	3.54	4.98	8.70

can be converted to a steel with end-[P] = 0.01-0.025%, without any difficulty. Two typical blows are given on p. 291⁴⁰.

The pig iron used in Linz & Donawitz contains 0.08-0.2% P and 0.2-1.0% Si, amongst other elements. As in the Thomas process, there is a distinct relationship between (Fe)-slag and P-metal (*cf.* Fig. 8.14). This figure also shows other values from the Kaldo, Rotor, PL, Thomas etc. processes. The (Fe)-slag is usually between 15-20% which is not abnormal for the open-hearth. The iron loss is not much since the slag bulk is about 120 Kg/t steel compared to 200-220 Kg in the Thomas process. The [P]-content is also lower, the higher the free lime. The latter is determined by subtracting the lime, forming mono-silicate and tetra-phosphate, from the total lime.

However, difficulty may arise with iron having more than 0.5%P. In such cases, the first slag is drained off when [P] \sim 0.5%. The [C]-content at this stage should not be below 1.5-2% since, during the second blow, a sufficient time must be given for melting the added fresh lime. [P]-contents of 0.025-0.030% can be reached at the end of the final blow. The second slag is retained in the converter and used as the first slag in the next blow, after suitable additions of lime, fluorspar, ore, etc. The slags obtained from iron with 0.5-1.3% P are not suitable for

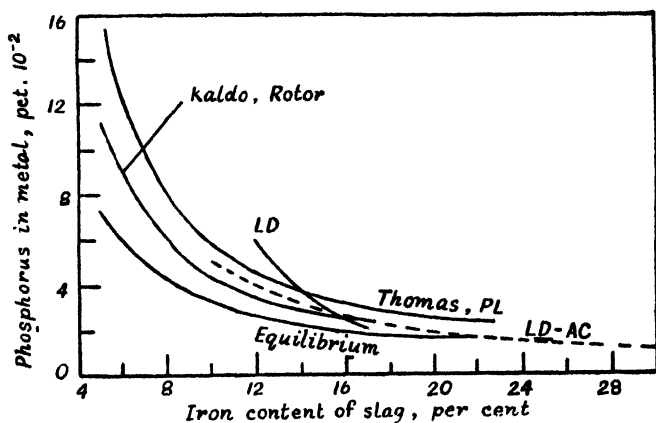


Fig. 8.14—Relation between phosphorus in metal & iron in slag in some steelmaking processes.

making fertilisers since the (P_2O_5)-content ranges from 5 to 10% only.

LD with Thomas iron 18, 44-49

The slag character and its influence on the end-[P] content is similar to that in the Thomas process. But the carbon can be held at any desired level. The slag should be very basic and saturated with lime if very low-[P] is aimed at. The rate of the process depends upon the amount of oxygen blown per unit time and also on the turbulence created by the carbon boil or, artificially, by the mild bottom-blowing of air or nitrogen. As in fine-dephosphorisation, the top-blowing needs a two-slag technique. Depending upon whether very soft or mild steel is desired, the first slag is tapped between 0.7-2% [C] (the lower and the higher carbon for the former and the latter varieties) with [P] \sim 0.2%. At these carbon contents the (Fe)-slag is low, about 10% FeO. Therefore, the iron loss in the first slag, which may be drained off through a tap-hole at the side of the converter, is not high. After the addition of more of lime, the metal is further blown with oxygen when low-[P] contents can be obtained. The second slag is high in (FeO), \sim 25-30%, and is retained for use as the first slag in the next blow. This minimises the iron loss and saves considerable oxygen, lime and heat. The first slag containing 20-25% P_2O_5 has ready market for the fertiliser industry.

It is possible to stop the first blow at high [C] and low [P], because dephosphorisation can be made to precede decarburisation by adjusting the lance height. If the oxygen jet is sharp and penetrating, the slag oxidation will be less and the carbon oxidation will increase, thereby decreasing the (Fe)-content of the slag by reducing the oxide. By lowering the lance, (Fe) can be brought down from 28% to hardly 5-6%. This also helps to reduce the foaming of the slag which is caused by the reaction of carbon, contained in the solid or viscous iron, with the highly oxidising slag.

Oxygen may also be blown through two or three concentric nozzles at different pressures so that the gaseous stream strikes both the metal and the slag. We know that because of lack of sufficient convection, it is difficult for the phosphorus in metal to reach equilibrium with the slag. With this arrangement, a

liquid slag suitable for phosphorus removal is formed easily and there is also sufficient bath action, through the carbon boil, for enabling the phosphorus atoms to reach the slag/metal interface. About 0.02% [P] can be easily attained.

LD-AC and OLP-processes ⁵⁰⁻⁵²

In the conventional LD, the initial iron oxide formed has to flux the solid lump lime which takes time. During this period some carbon is burnt off, before dephosphorisation starts. It is possible to start phosphorus oxidation earlier and at higher carbon level if lime powder is injected along with the oxygen jet. In this case, lime is made available at the very place where iron oxide is formed by the reaction of oxygen with iron and a highly oxidising and fluid basic slag is formed, capable of removing phosphorus immediately. This is the basic principle involved in the so-called LD-AC or OLP processes.

A sharp oxygen-lime jet increases decarburisation but, simultaneously, dephosphorisation also proceeds with sufficient velocity, so that phosphorus in steel reaches low levels before (or together with) the attainment of the desired C-content. The bath action is sufficient to enable the phosphorus to reach equilibrium with the slag (*cf.* Fig. 8.14). Since the removal of both the elements occurs simultaneously, the [O]-content is determined by [C] at the end of refining, as is the case in basic open-hearth, but the values are somewhat lower. For [C]-contents below 0.05%, the equilibrium curve of Vacher-Hamilton is approached (*cf.* Fig. 10.4).

The phosphorus contents reached at the first slag is 0.1-0.2% while carbon is still in the range of 0.7-0.8%. The second slag is retained for the next blow. The final [P] is between 0.01-0.02%. A typical LD-AC blow is shown in Fig. 2.11.

Buffer slag process ^{46, 47}

If the purpose of lime-injection is to obtain an early liquid highly oxidising basic slag, the same can be achieved by raising the lance when initially some iron has already been oxidised to FeO. Such increase in the height would make the oxygen jet strike on the slag rather than on the metal surface and the (FeO), originally formed, will be oxidised to Fe₂O₃, which, being a

better fluxing agent for lime, would liquefy it. Through agitation and diffusion the ferric oxide would come in contact with the metal and oxidise the phosphorus. This process suppresses the CO-evolution due to the lack of facilities for nucleation.

The 'buffer slag' process has the disadvantage that the refining takes a longer time. The carbon elimination is slow and, with the consequent lack of turbulence, the diffusion of phosphorus atoms to the slag/metal interface is also slow and its removal is thereby delayed. The elimination of both the elements can be accelerated if two jets could be available, one striking the metal and the other the slag surfaces. Such a double-lancing process, innovated at Mannesman, has had considerable success.

PL process³⁵

It is possible to produce good quality steel, e.g. for cold drawing purposes, with low-[P] and low-[N]. Thomas iron with ore and lime is initially blown as usual with air or oxygen-enriched air for 6-7 min when an intermediate is formed with 0.8-1.0% [P], and 0.002% [N]. Lime is also thereby liquefied to a certain extent. The converter is then brought to horizontal position, a water-cooled lance is introduced through the mouth and oxygen is blown at ~ 3.7 atm. pressure with the aim of impinging on the metal. When sufficient iron is oxidised for enabling the fluxing of lime, the lance is raised so that oxygen strikes the slag only and thus a rapid liquefaction of lime is ensured. During this period, some phosphorus and carbon are also eliminated but the metal and slag remain highly oxidised. Subsequently, the vessel is tilted vertically and re-blown. The turbulence causes extensive intermixing of metal and slag and the phosphorus is brought down rapidly to the usual Thomas metal level (cf. Fig. 8.14). The oxygen in metal lies higher than the equilibrium curve and follows more or less the open-hearth level above 0.05% [C]. Below this C-level, the oxygen crosses the equilibrium curve and assumes the value, usual in the Thomas metal.

Kaldo process⁵³

The various aspects of this process have already been discussed on pp. 33-38. It can be used for high, medium or low phosphorus iron. For the first variety, two or more slags may be necessary.

A major part of lime and ore is charged before starting the blow. The first slag is tapped off at 0.15-0.30% [P] and $\sim 1.5\%$ [C]. The (Fe)-slag is kept low ($\sim 4.5\%$), by adjusting the rotation rate for minimising the iron loss. Initially, the speed is kept moderate so as to obtain sufficient decarburisation as well as to maintain a high (Fe) in the slag, for effecting a simultaneous phosphorus removal. Thereafter, the rotation may be intensified for increased decarburisation and consequent lowering of (Fe). Low (Fe) at an advanced stage does not inhibit lime liquefaction, since an increasing (P_2O_5) in the slag is also capable of fluxing lime. A liquid, non-foaming slag is obtained which does not entrap the iron droplets. The second slag is tapped at a short interval when [P] $\sim 0.1\%$ and [C] $\sim 1\%$. The combined slag contains 15-20% P_2O_5 and is suitable for making fertilisers. A high speed at the end is necessary for increasing decarburisation and thereby decreasing the slag iron. Due to the turbulence caused by rotation, there is a closer approach to equilibrium than in the top-blown stationary converters. The chemistry of the process is, however, the same.

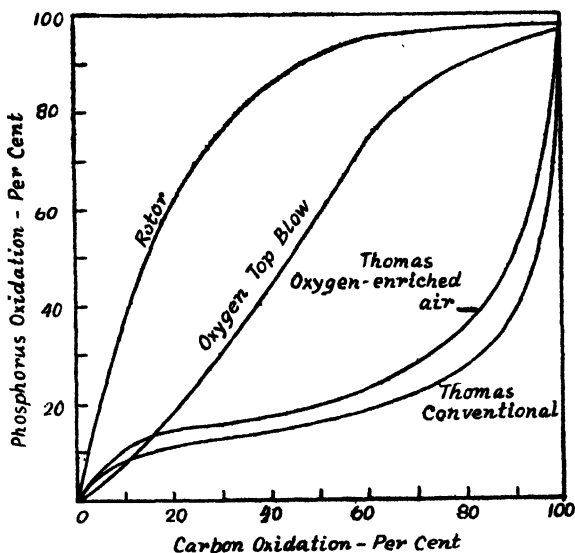


Fig. 8.15—Comparative rates of decarburisation & dephosphorisation in some steelmaking processes. (R. Graef, Stahl und Eisen, 77, 1957, 5).

Rotor process⁵⁴

The chemical principles and the physical influences of rotation were discussed on pp. 270-78. They are also clear from Figs. 2.10 and 8.15. Fig. 8.15⁵⁴ shows the comparative dephosphorisation and decarburisation rates in the Rotor and the top-blown converters as well as in the Thomas process with air and oxygen-enriched air.

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CHAPTER IX

THE REMOVAL OF SULPHUR

General ⁶¹

It has long been known that sulphur deteriorates the quality of steel. It imparts such undesirable properties as red-shortness, inferior surface characteristics, poor corrosion resistance and lower ductility. It is a problem to keep its amount to a low level in finished steel, especially now since at present the quality of the blast furnace raw material is deteriorating and low sulphur pig iron is made available to steel plants with great difficulty. Slags from the hot metal mixer and also lime and scrap contribute to the sulphur pick up in steel. In open-hearth steelmaking, apart from the slag and metal, the heating gases carry sulphur as well and much sulphur can enter the metal depending upon the furnace and the behaviour of the slag.

According to Hauck,¹ a 60 ton open-hearth melt heated by pulverised brown coal coke-oven gas containing 5.8 gm. S/m³ absorbed 26.2% from the gas. Koch and Fink² report that, in their experiments with radioactive sulphur, a 50 ton furnace fired with 54 gm S/100m³ of the gas showed a sulphur absorption in steel and slag of about 11—12%. Most of the sulphur pick up was during the 3½ hour meltdown period, when the heating gases swept directly over the solid scrap and the molten metal. The sulphur absorption is generally greater, the higher the initial S-content of the fuels.³

It is the aim of every steelmelter to keep the sulphur content in steel as low as possible, in the open-hearth lower than 0.05% S. Sulphur may be high, as much as 0.3%, for the free machining steels. It is neither cheap nor easy to remove sulphur if the initial sulphur in the metal is higher than the specifications. Its elimination depends upon various factors which must be kept under strict control. High temperature, increasing basicity and volume of slag and multiple-slagging all result in a better desulphurisation of steel but they entail longer heating and refining time, wear of the refractories, increased use of fluxes, increased loss of iron and manganese

in the slag. All these factors lead to a loss in the productivity and an enhanced cost of production.

In view of the above, it is necessary to find the most favourable conditions for the removal of sulphur to the slag during the making of steel. Sulphur occurs in iron as FeS which is soluble in liquid iron. Desulphurisation can only occur by the formation of insoluble sulphides or other sulphur compounds and their transfer to the slag. The formation of gaseous SO_2 is possible, but is without much importance in practice. A considerable sulphur removal has, however been attributed to such a phenomenon. In practice, lime is the base used for desulphurisation which, however, could be effected by any element whose affinity for sulphur is more than that of iron.

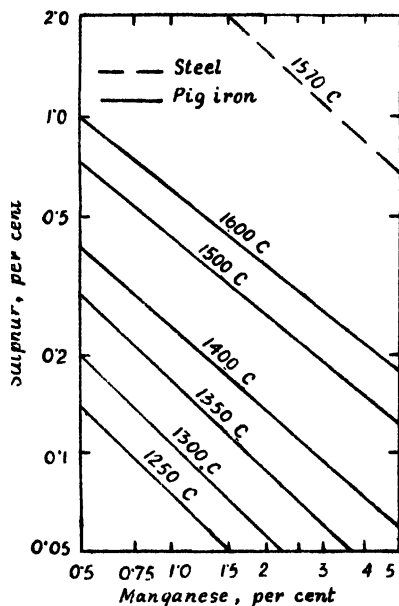


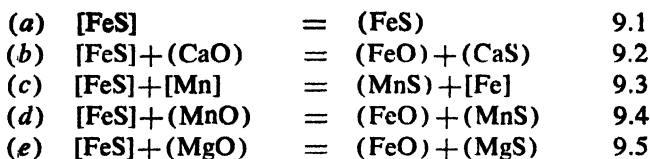
Fig. 9.1—Effect of manganese on sulphur content of liquid steel & pig iron. (J. Chipman, Basic Openhearth Steelmaking, AIME, Copyright 1951).

Manganese has a considerable desulphurising action, as shown in Fig. 9.1⁴. This is, however, with regard to the blast furnace iron. Manganese is soluble in iron and forms MnS or FeS-MnS which, because of low solubility, goes over to the slag. But calcium, being insoluble in iron, can only combine with sulphur at the

metal-slag interface which is only possible if either the sulphur diffuses from the metal to the interface or there is a thorough inter-mixing of metal and slag, as in the bottom-blown converters or in the open-hearth during the 'ore' or 'lime' boil.

The first thing in the slag-metal reaction is the knowledge of the equilibrium relations between the two regarding sulphur, the chemical reactions which take place leading to the transfer of sulphur from metal to slag or *vice versa* and whether the equilibrium is attained at all during the steelmaking process. In the open-hearth, because of the slowness of the process, there is more probability of the sulphur reactions between the metal and the slag reaching equilibrium than in the basic converter processes. The question of the acid process does not arise at all because almost no sulphur removal has been found to take place in acid slags.

It is conventional and convenient to denote the extent of sulphur removal by the ratio $(S)/[S]$. This distribution ratio increases with the slag basicity. Removal of sulphur in basic steelmaking processes can only result from any or all of the following equations:



The equilibrium constants of (b), (d) and (e), which show their relative desulphurising powers, are :⁵

$$\begin{aligned} \log K_b &= -2,047/T - 0.337; K(1,600^\circ\text{C}) = 37.10^{-3} & 9.6 \\ \log K_d &= -4,234/T - 0.271; K(1,600^\circ\text{C}) = 2.9.10^{-3} & 9.7 \\ \log K_e &= -7,530/T - 0.337; K(1,600^\circ\text{C}) = 0.046.10^{-3} & 9.8 \end{aligned}$$

There is a possibility of sulphur existing as sulphate instead of as sulphide in the slag⁶⁻⁸. According to Richardson and Fincham^{7,8} the sulphide forms below an oxygen-pressure of 10^{-6} atm. in the furnace atmosphere. At higher oxygen pressures, i.e. above 10^{-4} atm. the sulphur in the slag mostly exists as sulphate. They have shown, however, that the sulphate formation is not important in steelmaking processes.

Schenck⁹ is of the opinion that desulphurisation takes place according to Eqs. 9.2 and 9.3. The mass law when applied to them, however does not give satisfactory results even when (CaO) and (FeO) are calculated on the basis of his 'free-oxide' theory. The equilibrium constant rather varies with the SiO₂-content of the slag. Schenck's formula, obtained from the practical steel-making data and which contains constants with a temperature function together with the influence of Mn, free CaO and free FeO, is given below :

$$(S)/[S] \text{ (equilibrium)} = \frac{(S)_{Ca}}{[S] \frac{(CaO)}{(FeO)}} + \frac{(S)_{Mn}}{[S] \frac{[Mn]}{K_2}} = \quad 9.9$$

$$\text{where } K_2 = \frac{(CaO) [S]}{(FeO) (S)_{Ca}} \text{ and } \log K_2 = \frac{5,700}{3.72 + 0.05 (\% SiO_2)} - \frac{T}{\quad} \quad 9.10$$

$$K_1 = \frac{[Mn].[S]}{(S)_{Mn}} \text{ and } \log K_1 = \frac{-3,840}{T} + 1.17 \quad 9.11$$

(CaO) = free calcium oxide in slag in wt. %

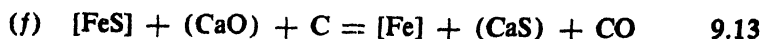
(FeO) = free ferrous oxide „ „ „

It is clear from Fig. 9.1 that the manganese, in amounts present in steel, does not play an important role. The effect of slag composition on Eq. 9.3 can also be neglected. It is evident that, in order to desulphurise by slags, a large amount of CaO is necessary. Therefore, Eq. 9.9 can be written approximately as :

$$\frac{(S)}{[S]} = \frac{(CaO)}{(FeO).K_2} \quad 9.12$$

Eq. 9.12 shows that a higher sulphur ratio is obtained as (CaO) increases and (FeO) decreases. In other words, a basic slag would facilitate sulphur removal under highly reducing condi-

tions, which result in a low iron oxide content of the slag. In an extreme case, as in the blast furnace where the slag is saturated with carbon, the over-all reaction for sulphur removal is obtained by the addition of the reaction of FeO and carbon with Eq. 9.2,



$$\log K_f = -4,130/T - 4.35; K(1,600^\circ\text{C}) = 141$$

It can be seen that K_f is about 4,000 times more than K_b . It appears that apart from the basicity, the iron-content of slag plays a vital role in the desulphurisation reactions.

Bardenheuer and Geller¹⁰ in 1934 carried on an extensive research, regarding the influence of various oxides on sulphur distribution, with slags containing FeO, CaO and Al_2O_3 in a high frequency furnace. Their results show conclusively that CaO, FeO, MnO, all play a part in desulphurisation; melts under pure FeO give a distribution value of 3.6 which increases with CaO and MnO, more so with the former. But, increasing the lime has a limit as it increases the viscosity of the slag which would require to be thinned by the fluorspar for obtaining a greater fluidity in order to facilitate the diffusion of sulphur. They conclude that, chemically, the fluorspar has practically no effect on the betterment of the ratio.

Maurer and Bischof¹¹ in 1936 gave a wide accumulation of results from data on acid and basic steel furnaces. They found that the distribution co-efficient, valid for [Mn] upto 0.6% and for slags with 35-41% CaO and 16-20% SiO_2 could be expressed as

$$(\text{S})/[\text{S}] = 2.0 + 10.0 [\text{Mn}]$$

For non-manganese steel, i.e. 0% [Mn],

$$(\text{S})/[\text{S}] = 2.0$$

Darken and Larsen¹² have derived an expression which is much more cumbersome than that of Schenck although it gives a fairly good agreement with the works practice. According to them, desulphurisation primarily follows Eq. 9.2 together with Eqs. 9.1 and 9.4,

$$(\text{S})/[\text{S}] = N \left[2.6 + 1.6 \frac{(\text{CaO})}{(\text{FeO})} \cdot (L-2) + 11.0\% [\text{Mn}] \right] \quad 9.14$$

where N = total number of moles in 100 gm of slag

$$= (n_{\text{CaO}} + n_{\text{MnO}} + n_{\text{FeO}} + n_{\text{SiO}_2} + n_{\text{P}_2\text{O}_5})$$

(FeO) = sum of all analytically determined FeO and Fe_2O_3 in the slag; one mole of $(\text{Fe}_2\text{O}_3) = 3(\text{FeO})$

$$\text{CaO}' = (\text{CaO}) - 4(\text{P}_2\text{O}_5)$$

$$L = \text{CaO}'/\text{SiO}_2$$

All quantities in the above are in moles except $[\text{Mn}]$, $[\text{S}]$ and (S) which are in wt%.

Eq. 9.14 shows that desulphurisation can only be carried out by lime if L is more than 2; in other words, if the quantity of lime is more than that required to form tetrphosphate and di-silicate. Eq. 9.14 recognises the experience of steel melters that high residual manganese and low (FeO)-slag help sulphur removal. The effect of temperature has been, however, disregarded.

Grant and Chipman¹³ also have found no effect of the temperature on desulphurisation between $1,500^\circ\text{--}1,650^\circ\text{C}$. According to them, the ratio $(\text{S})/[\text{S}]$ is alone a function of 'excess base', where the 'excess base' is determined from several assumed compounds they suppose to be present in the open-hearth slags. CaO , MgO and MnO are considered as bases and combine on a molar basis as : 1 mol: Fe_2O_3 , 2 mols: Al_2O_3 , 2 mols: SiO_2 and 4 mols: P_2O_5 . The mols of bases remaining after satisfying the acid constituents per 100 gms. of slag are termed the 'excess base'. The excess base in mol when plotted against $(\text{S})/[\text{S}]$ gives almost a straight line as shown in Fig. 9.2.¹³ It is found that variations in FeO (3-70%), CaF_2 (4-18%) and MnO (13-40%) do not affect the sulphur distribution ratio. It is clear that FeO acts as a mere diluent and $[\text{Mn}]$ (or MnO) has no direct effect on the sulphur ratio, which lead to the conclusion that desulphurisation in the open-hearth is due to simple partition of FeS according to Eq. 9.1.

The findings of Grant and Chipman that (FeO) and $[\text{Mn}]$ have no apparent effect on sulphur distribution are in direct contradiction to those of others. For the purpose of elucidating the action of FeO , Bishop, King and Grant¹⁴ used the results of several investigations and plotted $(\text{S})/[\text{S}]$ against base/acid ratio for different total (Fe)-contents. (See Fig. 9.3).¹⁴ The temperature range was $1,560^\circ\text{--}1,650^\circ\text{C}$ and the slag contained less

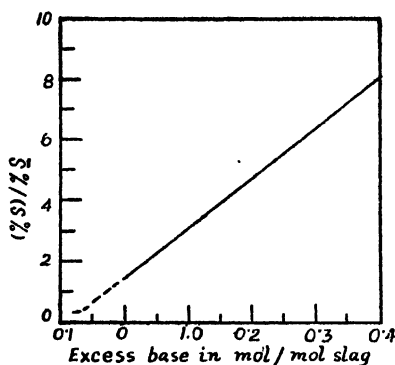


Fig. 9.2—Effect of excess base in slag on sulphur distribution ratio (N. J. Grant & J. Chipman, Trans. AIME, 167, 1946, 134-49).
[\underline{S} denotes sulphur in steel]

than 5% of Al_2O_3 or P_2O_5 which were regarded as equivalent to SiO_2 . Similarly CaO , MgO and MnO were each considered to be equivalent in their effect on the sulphur ratio. The total iron in the slag was converted into (FeO) . From Fig. 9.3, the sulphur ratio becomes better with increasing (FeO) below a basicity ratio of 2.7 and above this value the sulphur ratio increases with decreasing (FeO) . Around a basicity ratio 2.7, the desulphurising action is not affected appreciably with the change of FeO . With highly basic slags having ratios greater than 2.7, the desulphurising and oxidising powers are affected in the opposite direction by the varying FeO contents.

If the (FeO) -slag and, therefore, the oxygen potential of the slag and iron affect the sulphur distribution ratio, then, since the residual manganese in steel is a function of the oxygen potential of the slag and iron, it is to be expected that manganese should also influence the sulphur reactions. Therefore, the beneficial effect of high $[\text{Mn}]$ on sulphur partition is apparent, since only a low oxidising power of the slag can lead to a high residual manganese.

Harders, Grewe and Oelsen¹⁵ have shown that the influence of FeO on the sulphur ratio can be correlated with the manganese ratio since (FeO) -slag is a function of $(\text{Mn})/[\text{Mn}]$. That such a relationship exists in the open-hearth as well as in the laboratory melts is shown by the trend of the curves in Fig. 9.4 (a and

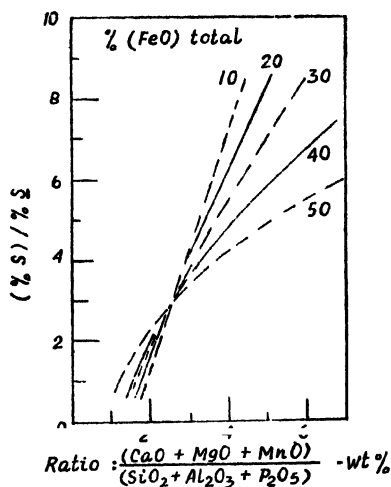


Fig. 9.3—Equilibrium sulphur distribution ratio as a function of slag basicity for constant total % (FeO). (From Blast Furnace & Steel Plant, Pittsburg, Pa.)
[S denotes sulphur in steel]

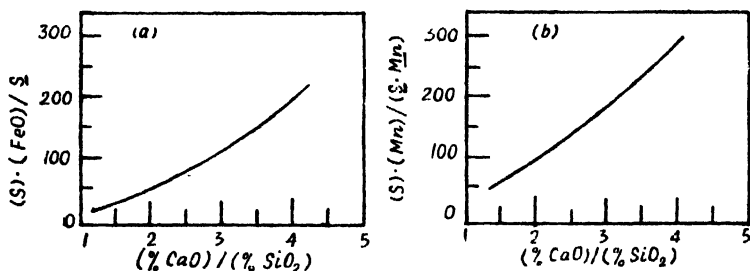


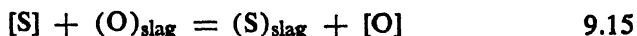
Fig. 9.4—Dependence of sulphur distribution ratio on (a) iron oxide content of slag and (b) manganese partition coefficient, at various slag basicities. (F. Harders, H. Grewe & W. Oeles, Stahl und Eisen, 71, 1951, 373-86).

[The underlined elements denote their presence in steel]

b), where the values of (FeO) in (*a*) has been replaced by (Mn)/[Mn] and drawn in (*b*). From (*a*), for the same basicity, the lower the (FeO), the higher the sulphur ratio; from (*b*), the higher the [Mn]/(Mn) i.e. the higher the [Mn], the higher is the sulphur ratio.

The connection between the (FeO) and the [Mn] in their effect has been ascribed above to the influence of the oxygen potential on the desulphurising capacity of slags. Carter¹⁶ believes that the

over-all reaction controlling sulphur removal from the metal to the basic slag proceeds according to



as suggested by Samarin, Temkin and Schwarzman.¹⁷

Since the supply of oxygen from the slag depends upon the excess base, the term (O) can be replaced by $\sum n_{MO}$ where

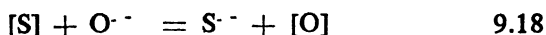
$$\sum n_{MO} = ({}^n\text{CaO} + {}^n\text{MnO} + {}^n\text{MgO} + {}^n\text{FeO} - 2{}^n\text{SiO}_2 - 3{}^n\text{P}_2\text{O}_5 - {}^n\text{Al}_2\text{O}_3 - {}^n\text{Fe}_2\text{O}_3) \quad 9.16$$

The equilibrium constant of the reaction of Eq. 9.15 being 0.021, we can write

$$\% (S) / \% [S] = 0.021 \cdot \sum n_{MO} / [O] \quad 9.17$$

Carter applied Eq. 9.17 and found that the experimental results of Grant and Chipman could be explained by this equation and that a plot of $(S)/[S]$ and $\sum n_{MO} / [O]$ approached linearity.

If it is assumed that the slag is dissociated, containing ions of different atoms or groups of atoms, then Eq. 9.15 can be written as



$$\text{and} \quad S^{\cdot -} / [S] = K \cdot O^{\cdot -} / [O] \quad 9.19$$

In view of the fact that the works data has to be applied to ascertain whether the Eq. 9.19 is valid, the oxygen content of the metal is required to verify it. But, generally, it is not available. To overcome the difficulty, Herasymenko and Speight¹⁸ combined the Eq. 9.19 with

$$[O] = (Fe^{++}) / A(O^{\cdot -})^{\frac{1}{2}} \quad 9.20$$

where A = a constant

Eq. 9.20 was obtained by them from a consideration of the reaction $Fe + O = Fe^{++} + O^{\cdot -}$. They found that

$$(S^{\cdot -}) / [S] = 0.043 \cdot (O^{\cdot -})^{3/2} / (Fe^{++}) \quad 9.21$$

Grant and Chipman found no effect of 3-70% FeO in the basic steelmaking slags. Rocca, Grant and Chipman¹⁹ carried on investigations on the effect of low- and high- FeO on desulphurisa-

tion. The results^{19,20} are given in Fig. 9.5 which shows the substantial variations in the desulphurising abilities of the basic open-hearth and basic electric furnace reducing slags and the blast furnace slags. The effect of low (FeO) content becomes obvious. The flattening of the curves in the neighbourhood of 3% FeO and above will be obvious from the consideration of [O] and from the oxide activity or oxide-ion activity of Eqs. 9.15 or 9.18.

The equations show the opposing effect of the oxygen in steel and the oxide activity of the slag. While an increasing oxide activity of slag should help in desulphurisation, it would mean a simultaneous increase of [O] which would tend to oppose the transfer of sulphur from metal to slag. It is probable that the constant level of desulphurisation at high FeO contents, as shown in Fig. 9.5, is due to these opposing effects cancelling one another.

The above is further confirmed by the work of Shanahan²¹ who plotted (S)/[S] against (FeO), maintaining a constant basicity. According to him, at low FeO, the desulphurisation is high, whereas the curve declines and maintains a more or less constant level over a large range at higher concentrations of FeO.

It is clear from what has been discussed in the preceding paragraphs that, at low concentrations of (FeO), the effect of the oxide-ion activity is paramount and the [O] plays a subdued role; while at higher (FeO)-contents, both the oxide-ion activity and the [O] must be taken into account. Since, it is the basic oxides which are the suppliers of oxygen-ions, the oxide-ion activity will increase with the increase of basic oxides. Hcrasymenko and Speight¹⁸ obtained a relationship between the (O^-) and the acid content ($\epsilon a = \% SiO_2 + 0.634\% P_2O_5 + 0.90\% Al_2O_3$) of the slag and prepared a nomogram from where the ratio (S)/[S] could be obtained from the known values of ϵa and (FeO). Although their nomogram gives reasonable agreement with the open-hearth data, it has been found to show a wide range of variation as well.

Further evidence from the laboratory experiments^{22,23} of the probable applicability of Eqs. 9.15 or 9.18 is discernible from a correlation of (S).[O]/[S] with the number of moles of acid constituents in the slag as shown in Fig. 9.6,^{14,24} where the silica and alumina have been taken as equivalent on a mole basis but only half as effective as P_2O_5 . Similar curves have been ob-

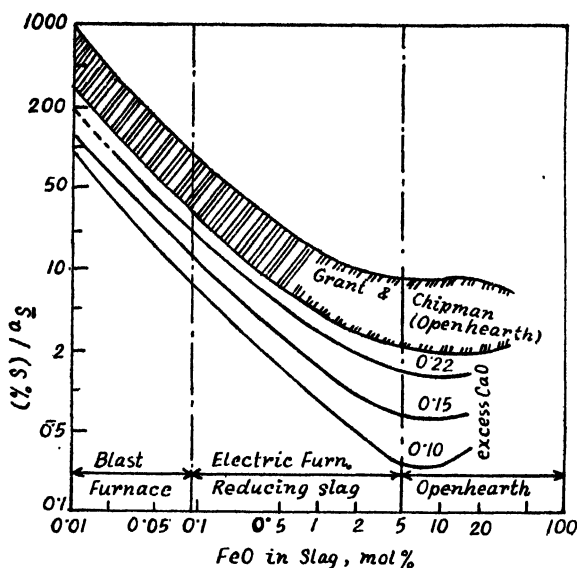


Fig. 9.5—Effect of iron oxide content on the desulphurising ability of iron & steelmaking slags. (J. Chipman, Metal Progress, 62, 1952, 97-107).
 [\underline{S} denotes sulphur in steel]

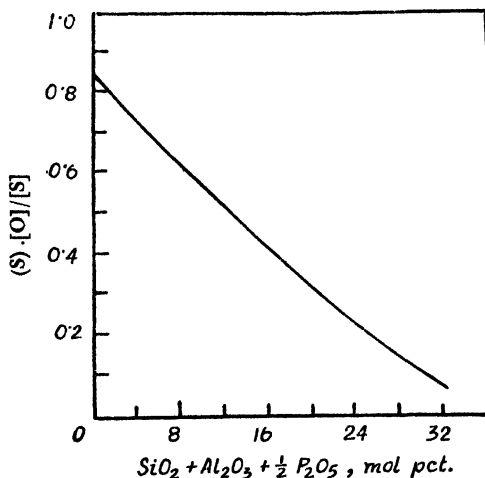


Fig. 9.6—Product of sulphur distribution ratio & oxygen content of metal as function of mol per cent acids in the slag. (From Blast Furnace & Steel Plant, Pittsburgh, Pa.)

tained (see Fig. 9.15) by Turkdogan²⁵ based on the data of a few British steel plants.

The attempts of the various workers, as enumerated in the foregoing discussions, have been to relate functionally the sulphur distribution with the oxygen-ion activity in an indirect manner. In order to substitute this activity, which cannot be determined experimentally, assumptions have been made of free oxides, excess base left after the formation of neutral compounds with acids and complete dissociation of slag constituents into specific ions. Turkdogan²⁶ attempts to circumvent the necessity of finding the oxygen-ion activity by introducing *sulphur capacity* in the following equation, obtained from Eq. 9.15 :

$$K = \frac{a_{(S)} \cdot a_{[O]}}{a_{[S]} \cdot a_{(O)}}$$

For any given slag composition, the oxygen-ion activity $a_{(O)}$ may be considered as constant and the sulphur in the slag may be supposed to behave ideally at low concentrations, usually found in practice. Therefore K can be written as :

$$k_S = N_{(S)} \cdot a_{[O]} / a_{[S]}$$

where $N_{(S)}$ = ion fraction of slag sulphur

$a_{[O]}$ = oxygen activity in metal ($= f_O \cdot \%[O]$)

$a_{[S]}$ = sulphur activity in metal ($= f_S \cdot \%[S]$)

k_S = sulphur capacity of slag

But, since $a_{(O)}$ is influenced by the slag composition, k_S must also be a function of slag composition. According to Turkdogan, k_S is simply related to the so-called sulphur capacity index λ by

$$\lambda = 1 / (N_{SiO_2} + 1.5 N_{P_2O_5} + 1.5 N_{Al_2O_3}) \quad 9.22$$

The complete equation including the effect of temperature on is given by

$$\log k_S = \frac{-3,380}{T} - \frac{2.68}{\lambda + 0.4} + 0.11 \quad 9.23$$

In deriving the above equation, Turkdogan could not discern any effect of the relative proportions of the basic oxides, CaO, MgO, MnO, etc, which agrees with the statement of Grant and Chipman that these bases are equivalent on a mole per mole basis as far as the sulphur reaction is concerned. Further, the fluoride ions do not affect the sulphur capacity.

From known temperature, slag composition and, therefore, λ we can find k_S from Eq. 9.23. Again, if %[O] and f_O are known, $a_{[O]}$ can be determined; otherwise, the value of $a_{[O]}$ can be evaluated from the isoactivity diagram of Turkdogan and Pearson (*cf.* Fig. 4.4) and the slag composition. Thus, for any given value of $N_{(S)}$ and slag composition, we can find $a_{[S]}$ from where %[S] is derived if f_S is known :

$$\%[S] = a_{[S]} / f_S$$

Now, from the known analysis of the metal, f_S can be determined with the help of Wagner's equation (*cf.* p. 8).

Thus, for any given temperature and slag and metal compositions, we are in a position to derive, theoretically, the sulphur content of the metal. A comparison between %[S] thus determined and that found from the analysis, during refining and tapping of the basic open-hearth heats, shows that both are identical and, therefore, an equilibrium between sulphur in the slag and that in the metal during basic open-hearth steelmaking is actually attained. Similarly, others have used *sulphide capacity*.^{7,8,27}

Apart from the chemical reaction, the physical factors for an efficient sulphur removal must not be under-estimated. Since the slag-metal reactions are heterogeneous in character, the diffusion of sulphur from the metal to the slag/metal interface and the diffusion of slag sulphur away from the interface assume importance. Therefore, a fluid slag is helpful to sulphur removal. Superior desulphurisation at higher temperatures is not so much due to the higher chemical reactivity as to the greater fluidity of the slag. Also the greater the slag/metal interfacial area, the more will be the transference of sulphur to the slag. Thus, an intimate mixing (as caused by the 'boil' in open-hearths and the

blast in converters) between the slag and the metal is a necessity.

The results obtained from the laboratory experiments concerning sulphur distribution are, however, vitiated by the reaction of a third (gaseous) phase in the open-hearth. The fuels used for firing these furnaces invariably carry sulphur which takes part in the gas/slag reactions. They may contain as much as 3% sulphur, sometimes more, which when burnt in the furnace comes into contact with the metal and slag, mostly in the form of H_2S and SO_2 , the latter being predominant in an oxidising atmosphere (as prevails in the furnace). The reactions of the metal with these two sulphur bearing gases have been discussed on p. 134. The conclusions drawn there do not strictly apply in the open-hearth since the slag layer acts as a buffer between the metal and the heating gases. Of course, after the melt-down period and the floating of lime, the latter, being a basic oxide, helps sulphur pick-up. Although, according to Carter and Tahir²⁸ 1-6% oxygen in the furnace atmosphere should not affect sulphur pick-up by the molten metal, in practice, however, it has been found that the pick-up is greatly suppressed, even in the melt-down period, if the heating gases are oxidising. This is probably because of the formation of an oxide-rich slag serving as a protection from the sulphurous atmosphere.

It is to be noted that the entire fuel sulphur does not necessarily enter the furnace atmosphere. Those fuels, which are preheated, lose considerable amount (30-70%) of their sulphur to the ingoing checker works which contain deposits of CaO , MnO , FeO (retained from out-going waste gases carrying these particles in the previous cycle) capable of retaining sulphur as sulphides.^{9,29,30} From a theoretical calculation of the action of sulphur-bearing gases on solid CaO , MnO and FeO , Schenck⁹ suggests that the transfer of sulphur from the gas to the solid phases is favoured by low temperatures and reducing conditions (i.e. high CO/CO_2 ratio in the gases). There is an optimum desulphurising temperature depending upon the CO/CO_2 ratio. As the latter decreases, the optimum temperature also decreases. According to Eisenstecken and Schulz,²⁹ the optimum temperature lies between 1,000-1,100°C. The retention of sulphur is limited, evidently, by the availability of the basic deposits.

These sulphide deposits do not remain as such after the reversal, i.e. when the waste gases are allowed to pass through the checker under discussion. During this period, the oxidising gases convert them to sulphates which decompose at the prevailing high temperatures. The results of Eisenstecken and Schulz, however, show that all the sulphates are not removed and some are left in the checker which, on reversal, may enter the furnace with the ingoing air.

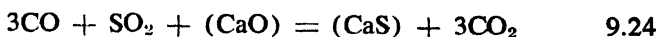
The calculations of sulphur balance from the total sulphur in the charge and the fuels show that a considerable sulphur pick-up by the metal takes place, especially when using a high-sulphur fuel. On the other hand, there is the possibility of sulphur escaping to the gas phase when using low-sulphur or sulphur-free fuels such as natural gas. Harders *et al*¹⁵ also found that whether the metal would gain or lose sulphur, depended on the amount of sulphur in the fuel and the charge.

It is the universal opinion now that sulphur pick-up from the furnace gases occurs mostly during the charging and melting periods. This finds new support from the extensive works of Harders *et al* which show that, with the increase of fuel sulphur, there is a simultaneous increase in the total sulphur of the slag and metal at melt-down. The tapping sulphur, [S], depends on the melt-down sulphur, although there is some influence of the fuel sulphur on metal-sulphur during the refining period. Harders *et al* are also of the opinion that the melt-down sulphur assumed limiting values, depending upon the sulphur in the heating gases, during charging and melting. This means that it is immaterial whether low or high sulphur charge is used in the furnace, since [S] at melt-down is largely determined by S in the gases. It is unlikely that the sulphur in the initial charge would be without importance, especially when large quantities of hot metal are used. However, their work and that of Carter and Tahir show that considerable pick-up is possible from the heating gases if the metal is exposed to the gases for a sufficiently long period. Light scrap with large surface area will particularly be affected by high sulphur gases.

We have seen that under both reducing and oxidising conditions, the metal is susceptible to sulphur pick-up from the gases. This may happen mainly during charging and melting since, after

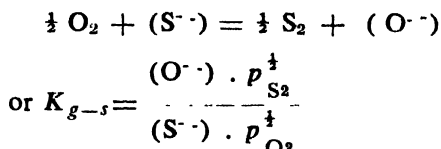
the clear melt, the metal is covered with a slag layer. Thereafter, the gas-slag reaction must assume importance as the metal is no longer in direct contact with the gases. Loss of sulphur from the metal to the gases after melt-down can only occur through the slag phase.

Both Herty⁸¹ and Schenck⁹ agree that CO evolved during the carbon boil helps the slag lime in reducing SO₂ in the gases to form CaS,

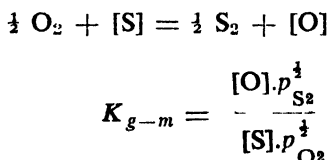


It would be expected that, during the lime-boil, the oxidising CO₂ gas evolved should reverse the reaction, i.e. slag sulphur should escape to the gases. This is also the opinion of some.

Richardson and Withers⁶ have also shown, from theoretical calculations, that reducing conditions and high gas-sulphur favour sulphur pick-up by the slag. They assume the gas-slag reaction to take place as :



and the gas-metal reaction as :



By co-relating the two equilibrium constants and with the values of [O] and [S] as per analysis for metal in equilibrium with the slag, they have drawn a diagram (Fig. 9.7)⁶ showing the relationship of the oxygen potential (in the form of CO/CO₂ ratio, which means the degree of combustion) and the sulphur content of gas for two levels of sulphur in metal in equilibrium with two different slags. The lines A and B represent two sulphur levels of slags A and B, corresponding to 0.01% and 0.1% of sulphur

in the metal respectively. The lines show that, at high sulphur in the gas and low CO_2/CO ratio (reducing condition), the slag will pick up sulphur and *vice-versa*. It is clear that, under oxidising conditions, the metal and slag can tolerate high sulphur

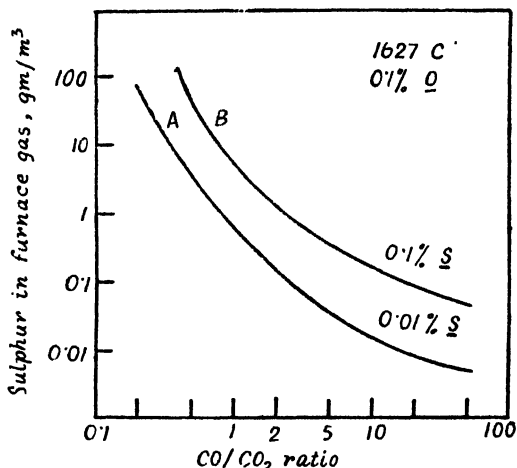


Fig. 9.7—Calculated relationship between the degree of combustion (CO/CO_2) and sulphur content of furnace gases in equilibrium with basic slag at 1,627°C. (F. D. Richardson & G. Withers, J. Iron Steel Inst., 165, 1950, 66-71).

[S and O denote their presence in steel]

in gas. For example, line A shows that a slag in equilibrium with 0.01% [S] can tolerate 0.013 gm S/ m^3 in a gaseous atmosphere with $\text{CO}/\text{CO}_2=10$. If the combustion degree is increased, e.g. $\text{CO}/\text{CO}_2 = 1$, the same slag can tolerate 0.56 gm S/ m^3 without any sulphur pick-up. An increase of sulphur in the gas will mean sulphur pick-up by the slag, which will be in equilibrium with higher % [S] in the metal. Thus, for example, the state of B is attained with 5 gm S/ m^3 in gas at $\text{CO}/\text{CO}_2 = 1$, which corresponds to 0.1% [S]. Temperature too has its effect. High temperature and high CO_2/CO ratio increase the tendency of the slag to lose sulphur to the gas.

Basic open-hearth

We have discussed in the preceding sections the beneficial influence of high basicity, low iron oxide, low viscosity of the slag

and that of high bath temperature on sulphur removal. It has also been mentioned that the results of sulphur equilibrium experiments in the laboratory are not directly comparable with the actual works data, because of the participation of the gaseous phase which can exchange sulphur with the bath. It is, therefore, convenient, as has been done in the preceding pages, to use the sulphur distribution ratio $\eta_S = (S)_{\text{slag}} / [S]_{\text{metal}}$ and determine the conditions which give higher η_S . A knowledge of the equilibrium ratio $\eta_S (\text{equi}) = (S) / [S] (\text{equi})$ is still useful, because the transfer of sulphur from metal to slag can only occur when the equilibrium sulphur ratio is greater than the actual ratio, η_S , and measures can be taken, if possible, regarding the slag composition, viscosity, temperature etc. to improve upon η_S . It is evident, however, that a comparison of the η_S values is not above criticism, since η_S can be high if the slag absorbs a considerable amount of sulphur from the heating gases with a simultaneous transfer of the sulphur, proportionately less, to the metal.

A high efficiency of sulphur removal can be expected if the slag composition and the temperature favour a high value of $\eta_S (\text{equi})$. The transfer of sulphur from metal to slag may be delayed due to slow diffusion, if the slag is viscous, even when a vigorous boil ensures a thorough mixing of the two phases and the slag is chemically favourable for desulphurisation. Addition of fluorspar increases the fluidity of the slag and thereby accelerates the rate of desulphurisation. Sometimes, the slag shows a heterogeneous character with regard to sulphur distribution, the cause probably being the interaction of the gas with the slag. An increase in the slag bulk also greatly facilitates sulphur removal. Since η_S is a ratio of wt. per cent of sulphur in slag to that in metal, it is evident, in order that the ratio remains constant, the amount of sulphur in slag will be larger when its bulk is high.

Schenck⁹ has produced Fig. 9.8 for desulphurisation by way of lime for different (ΣFe), (ΣCaO), (ΣSiO_2) and (ΣMnO) contents of slag at different temperatures. Neglecting the effect of Mn on sulphur removal, the equilibrium formula used (*cf.* Eq. 9.12) is :

$$\eta_S (\text{equi}) = \frac{(\Sigma S)}{[S]} = \frac{(\text{CaO})}{(\text{FeO}).K_2}$$

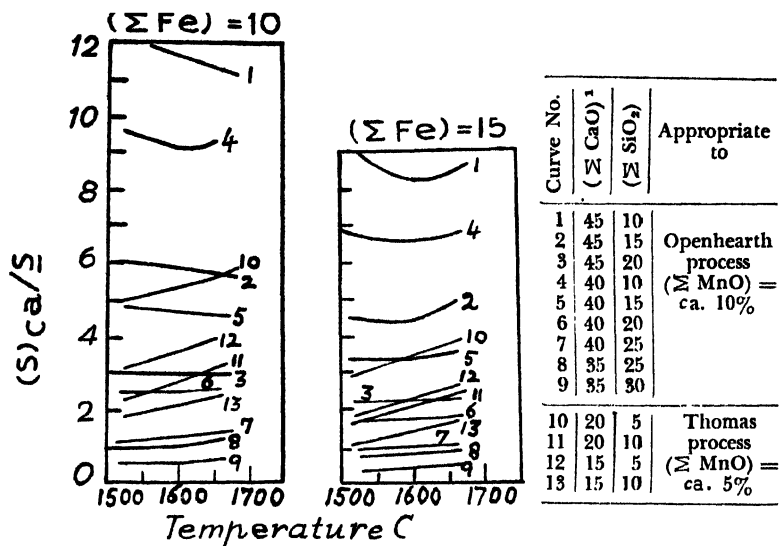


Fig. 9.8—Equilibrium positions for lime desulphurisation in basic steel-making processes. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).
[S denotes sulphur in steel]

The different contents of lime and silica and (MnO) for each curve are given in the appended table of the figure. Some curves in the figure are applicable to desulphurisation in the basic bessemer as well. This figure, whether it has any theoretical basis or not, is applicable to slags within the composition range of the basic open-hearth and Thomas processes.

The figure shows that the sulphur ratio is higher

- the lower the (ΣFe) —content of the slag.
- the lower the (ΣSiO_2) —content of the slag.
- the higher the $(\Sigma \text{CaO})'$ —content of the slag.
- the lower the $(\Sigma \text{P}_2\text{O}_5)$ —content of the slag since

$$(\Sigma \text{CaO})' = (\Sigma \text{CaO}) - 1.57 (\Sigma \text{P}_2\text{O}_5).$$
- the higher the (ΣMnO) content of the slag.

The effect of the temperature is peculiar. Thomas slags shows a continuous increase in the sulphur ratio with temperature

while some of the open-hearth slags having the same composition show a minimum in the ratio in the neighbourhood of 1600°C .

An increasing amount of (ΣMnO) has a small but definite favourable effect. According to Schenck, it is due to the simultaneous increase of free lime. Recently, the influence of $[\text{Mn}]$ and (MnO) on desulphurisation has been extensively studied, from numerous actual open-hearth heats, by Speith, Vom Ende and Mahn⁸². The relationship between $[\text{S}]$ and $[\text{Mn}]$ during the melting period follows the same pattern as Fig. 9.1, i.e. the higher the $[\text{Mn}]$ and lower the temperature, the lower the $[\text{S}]$. They could not find any influence of $[\text{C}]$ and melting time on the $[\text{Mn}]/[\text{S}]$ relationship. However, the situation completely alters while refining, when desulphurisation worsens during the reduction of manganese. Sulphur removal improves as $[\text{Mn}]$ is oxidised away

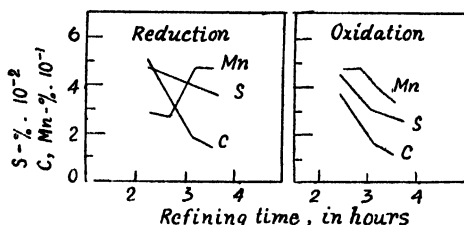


Fig. 9.9—Course of sulphur removal during oxidation & reduction of manganese in basic openhearth. (K. G. Speith, H. v. Ende & G. Mahn, *Stahl und Eisen*, 78, 1958, 27-34.)

to the slag (see Fig. 9.9). This peculiar phenomenon could be explained by the changes in the slag composition during refining. It is known that the sulphur ratio increases with the free lime as shown in Fig. 9.10. The free lime increases, as is seen in the same figure, with the iron content (ΣFe) of the slag. Therefore, an increasing (ΣFe) should increase desulphurisation in so far as it helps to bring more lime into solution and thus increase the free lime. But, since a higher (ΣFe) results in an increased oxidation of $[\text{Mn}]$, therefore, it is inferred that the Mn-oxidation should increase desulphurisation. The free lime in Fig. 9.10 has been estimated as $(\text{CaO}_{\text{free}} = \Sigma \text{CaO} - \text{CaO}_2\text{CaO} \cdot \text{SiO}_2)$.

The decrease in $[\text{S}]$, during and after refining, with an increasing (ΣFe), can only be attributed to the increase of free lime or its activity, caused by the fluxing action of (FeO) . According to

Eq. 9.2, an increased oxygen potential of the slag retards sulphur transfer from the bath. Therefore, an increased desulphurisation by the increasing (Σ Fe) can only be possible³³ either because (i) the ferrous-oxide activity of the slag (a_{FeO}) actually decreases with the dissolution of lime, or because (ii) even if the a_{FeO} increases, its deleterious effect is more than offset by the much stronger favourable effect of the increasing lime activity.

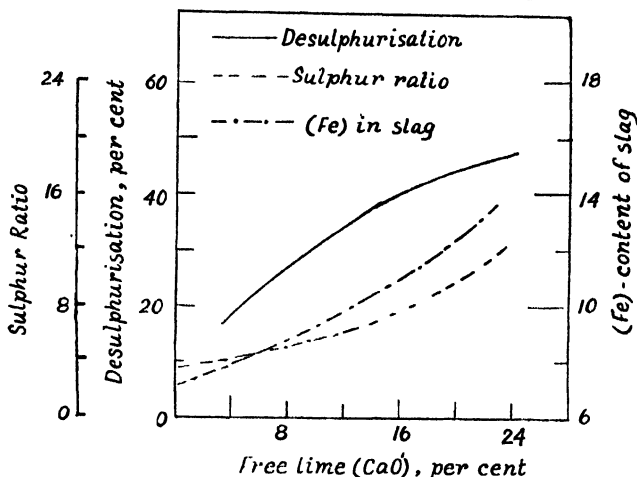


Fig. 9.10—Dependence of desulphurisation, sulphur ratio & Fe-content of basic openhearth slag on free lime. (K. G. Speith, H. v. Ende & G. Mahn, *Stahl und Eisen*, 78, 1958, 27-34.)

The maximum lime activity ($a_{\text{CaO}} = 1$) will naturally be exhibited when it is pure, but it is impossible to obtain it in the liquid state at steelmaking temperatures because of its high melting point, 2,580°C. But the attainment of a lime activity of the order of pure lime is feasible, according to the laws of heterogeneous phase equilibrium, if pure lime is in equilibrium with a lime-saturated slag. Such a slag is obtainable in the basic open-hearth when the CaO/SiO_2 ratio is about 4, as shown in Fig. 9.11b. In this quasi-ternary figure, the sum of the concentrations of CaO , SiO_2 and FeO have been converted to 100%. The full line shows the saturation limit of lime at about 1,700°C, which is similar to that found by others. The dotted line denotes a $\text{CaO}/\text{SiO}_2 = 4$ and it runs approximately along the saturation curve. It is, therefore, possible to obtain a maximum lime activity in a liquid slag

along the saturation curve, if $\text{CaO}/\text{SiO}_2 = 4$. In the open-hearth, the initial high silica slag is diluted by the continuous dissolution of lime and the addition of iron ore. As long as the saturation line is not reached, the continuous increase in the basicity ratio increases sulphur removal which is at its highest, as shown in Fig. 9.11*a*, at $\text{CaO}/\text{SiO}_2 = 4$. Fig. 9.11*a* shows that desulphurisation or sulphur ratio decreases above this basicity. This can only be explained by the fact that the (FeO) adversely affects sulphur removal after the ratio is surpassed and an increasing FeO is necessary to keep the slag fluid at a higher basicity. The mode of action of (FeO) in the removal of sulphur may be gathered from Fig. 9.11 (a), (b) and (c). Figure (a) shows the change in the sulphur ratio with increasing CaO/SiO_2 ; the simultaneous change in the slag composition is drawn in (b), which is the quasi-ternary $\text{CaO}-\text{SiO}_2-\text{FeO}$ system; whereas (c) shows the same changes in the slag, in the (FeO)-activity diagram of Turkdogan and Pearson (Fig. 4.4).

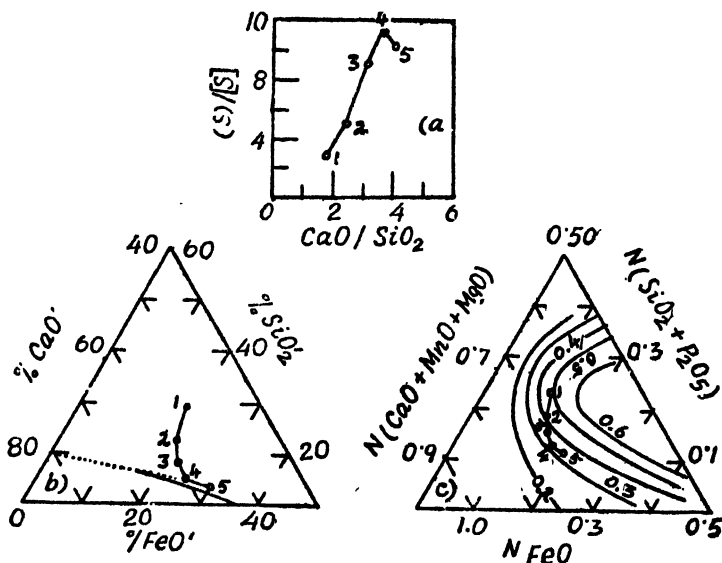


Fig. 9.11—Relationship between sulphur distribution ratio and compositional changes & FeO-activity of basic openhearth slags. (K. G. Speith, H. v. Ende, F. Bardenheuer & G. Mahn, *Stahl und Eisen*, 79, 1959, 926-33).

Desulphurisation is most favourable when the slag approaches the lime-saturation curve (compare *a* and *b*). Further increase in the basicity ratio and (FeO) worsens sulphur removal. Figure (c) shows that the a_{FeO} , which decreased as the slag composition was approaching saturation, starts increasing as the slag becomes enriched with (FeO) along the saturation line. Since the lime-activity remains constant once the slag becomes lime-saturated while the a_{FeO} increases, desulphurisation starts being affected adversely. It is clear that the highest sulphur ratios can be obtained when the slag is liquid and lime-saturated ($\text{CaO}/\text{SiO}_2 = 4$), i.e. when the slag exhibits its highest lime-activity and lowest (FeO)-activity. On the attainment of lime-saturation, the slag is incapable of further sulphur removal except by an increase in its bulk. For this purpose, lime has to be increased which, in its turn, would require more silica so as to maintain the most favourable lime-silica ratio of 4. This is an example where an increase of acid silica can help in the removal of sulphur.

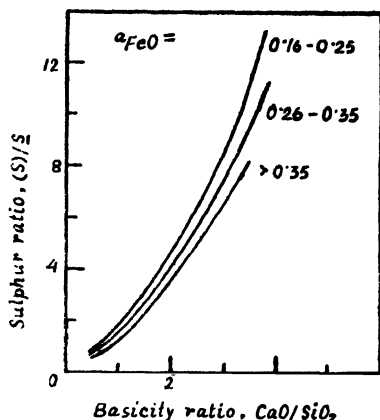


Fig. 9.12—Dependence of sulphur distribution ratio on lime-silica ratio & FeO-activity of basic openhearth slags. (K. G. Speith, H. v. Ende, F. Bardenheuer & G. Mahn, *Stahl und Eisen*, 79, 1959, 926-33).
[S denotes sulphur in steel]

The change in slag composition is of importance for desulphurisation; for, the lime-saturated slag may be attained with a higher or lower (FeO)-activity according as the composition inclines towards the FeO-corner or the (CaO)-corner of the iso-activity

diagram, Fig. 9.11(c). The adverse influence of a high a_{FeO} on sulphur removal is shown in Fig. 9.12.³³ This work of Speith *et al*³³ corroborates that desulphurisation follows equation 9.2, since sulphur removal from the bath to slag is greater, the lower the a_{FeO} and the higher the a_{CaO} .

The influence of silica on sulphur removal is such that the higher the silica content of the slag, the lower is the lime-activity and, therefore, the worse is the desulphurisation (except when the slag is already lime-saturated and a further increase of lime would need more SiO_2 , so that $\text{CaO}/\text{SiO}_2 = 4$, for the liquefaction of the slag).

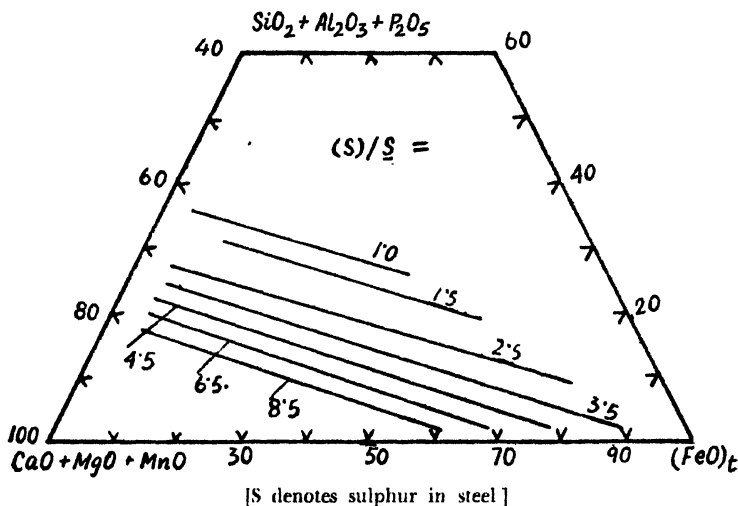


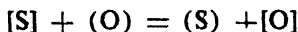
Fig. 9.13—Equilibrium sulphur distribution ratio as a function of composition of basic slags containing small amounts of MnO , Al_2O_3 and P_2O_5 . (From Blast Furnace & Steel Plant, Pittsburgh, Pa.)

It is of not much use to know the sulphur ratio if the results are not reproducible, or the results of one series of furnace experiments are not applicable to other furnaces under similar conditions, or if the ratios vary from heat to heat, or the equilibrium is not reached in the same furnace itself during refining, or the attainment of the equilibrium is delayed due to additions, etc. Speith *et al*³² have drawn the sulphur ratios on a quasi-ternary diagram for different slag compositions obtained during refining and directly before tapping in numerous basic open-hearth heats.

The lines of equal (S)/[S] ratios run approximately from a composition of $2\text{CaO}.\text{SiO}_2$ towards the (FeO) corner. These lines fit in approximately with those of Fetters and Chipman,²² obtained during laboratory experiments with artificial slags (*cf.* Fig. 9.13),¹⁴ The experiments of others^{10, 15} also show similar sulphur ratios. It can be reasonably assumed that sulphur distribution between the bath and slag in the basic open-hearth approaches equilibrium, both during and at the end of refining. The results of Trentini *et al*⁸ and Speith *et al* both add weight to this belief. They show from numerous open-hearth melts that the sulphur ratios of any two melts of approximately the same slag composition are nearly the same, irrespective of whether the sulphur ratios were high or low.

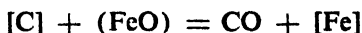
In view of the above and also the fact that the sulphur ratio rises simultaneously with the basicity, it is clear that the sulphur equilibrium between the metal and slag adjusts rapidly according as the slag composition changes. Further proof of this can be had from the fact that the sulphur ratio rises as long as the slag is unsaturated with lime, inspite of the rise in (Σ Fe); but, as soon as the saturation is reached, the worsening of desulphurisation starts. This can only mean that the bath and the slag strive to attain equilibrium with regard to sulphur which is very sensitive to any change in the slag composition. It follows, therefore, that, in dealing with a high sulphur charge, it is necessary to attain the lime saturation as quickly as possible in order that the refining period is not unduly extended. This can be achieved by any fluxing agent that not only increases the fluidity of the slag but also dissolves the lime rapidly, so as to reach saturation. Such a flux is the universally used fluorspar, a proper use of which can achieve the purpose. On the shop floor the basicity can be easily measured by the conductivity of an aqueous solution of the slag.^{21, 15}

Turkdogan²⁵ has attempted to produce the basic relationship between the slag and metal compositions regarding desulphurisation, for the purpose of finding a practicable method of slag control. He also proposes that during desulphurisation, the sulphur from the metal migrates to the slag with the simultaneous transfer of oxygen from slag to metal.



The equation shows that desulphurisation is thwarted by oxidising conditions in the metal.

Instead of calculating the oxidising power of the slag, which is the same as the $(\text{FeO})_t$ -activity, from the slag composition and Fig. 4.4, he considers the oxidation of carbon



as a more useful measure. The carbon should determine the a_{FeO} or the oxidising power of slag under given conditions, if the reaction reaches equilibrium. But, it has already been shown that, under the open-hearth steelmaking conditions, this reaction does not reach equilibrium because of the nucleation factors. Nevertheless, from numerous heats in English steelmaking companies, Turkdogan could deduce that, for a given $[\text{C}]$, the slag composition varies in a regular manner. He has produced a pseudo-ternary diagram where iso-carbon curves are drawn as functions of the slag compositions (see Fig. 9.14).²⁵ A study of the curves shows (i) for a given (FeO) -slag, the oxidising power of the slag—expressed through $[\text{C}]$ —increases, i.e. $[\text{C}]$ decreases, as the acidity ($\text{SiO}_2 + \text{P}_2\text{O}_5$) of the slag increases, (ii) for a

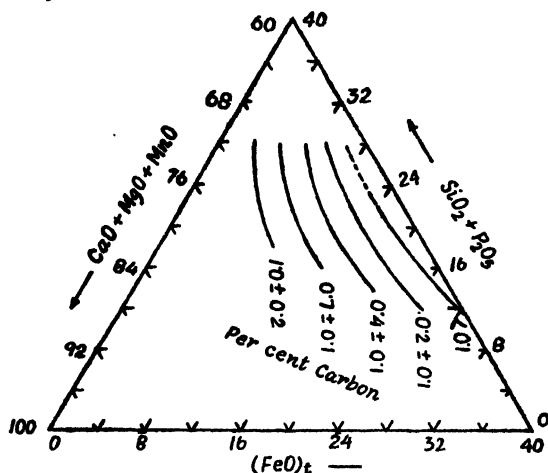


Fig. 9.14—Iron oxide iso-activity lines of basic slags expressed in terms of carbon content of metal. (By courtesy of Steel & Coal.)

given acidity, the oxidising power increases or $[\text{C}]$ decreases as (FeO) increases, (iii) for a given basicity ($\text{CaO} + \text{MnO} + \text{MgO}$),

a replacement of acids by (FeO) does not change the oxidising power or the [C]-content appreciably. It can therefore be concluded that within the ranges of basic open-hearth slags, a lower [C] requires a higher iron-oxide and/or, acid in the slag.

Now, in order to correlate the above findings with desulphurisation, he uses the following expressions :

$K(O) = \text{sulphur capacity} = (S) \cdot (\Sigma Fe) / [S]$, which is obtained from the equilibrium constant of the Eq. 9.25, and

$$K(O) = (S) \cdot [O] / [S] \quad 9.26$$

The transfer of sulphur from metal to slag, represented by Eq. 9.25, is not favoured under oxidising conditions; therefore, for a given (ΣFe) , the value of sulphur capacity will decrease with increase in the oxidising power of the slag.

Since an increasing acidity increases the oxidising power of the slag, it is clear from Eq. 9.26 and what has been said in the preceding paragraphs, that the sulphur capacity decreases with increasing $(SiO_2 + P_2O_5)$. The effect of acids on the sulphur capacity has been combined in Fig. 9.15²⁵, for various melts from different steelmaking units, where $(SiO_2 + P_2O_5)$ is related to (S).

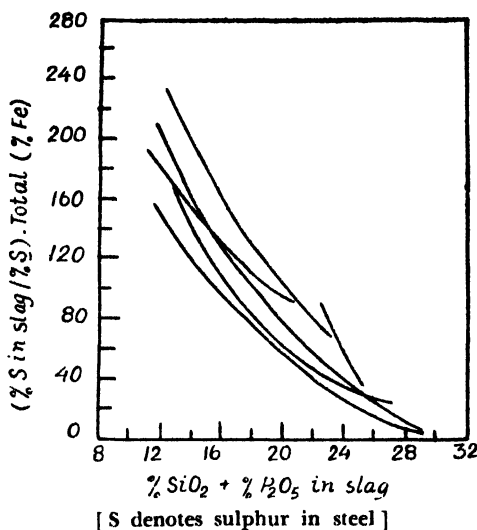


Fig. 9.15—Data from various openhearth works relating sulphur with acids in slag. (By courtesy of Steel & Coal.)

$(\Sigma \text{Fe})/[\text{S}]$. From Figs. 9.14 and 9.15 it can be roughly estimated, what should the total iron- and acid-contents of the finishing slag be for any desired sulphur ratio and final $[\text{C}]$ -content. In view of the spread of the results in Fig. 9.15, it is advisable for each basic furnace to construct its own curves similar to Figs. 9.14 and 9.15.

Effects of slag bulk

The effects of slag bulk and multiple slagging have been discussed on p. 169. Assuming an initial sulphur of 0.06% $[\text{S}]$ and a maximum desulphurisation at $\text{CaO}/\text{SiO}_2=4$, Fig. 9.16³³ has been drawn, giving the residual sulphur in the basic open-hearth metal for different quantities of slag. As for example, to reach 0.038% $[\text{S}]$, about 5% slag of basicity ratio of 4 is needed; whereas, for almost the same end-sulphur and a basicity ratio 2.5, the slag bulk should be 10%. But to reach 0.015% $[\text{S}]$ at ratio 4, the bulk must be 25% which is impossibly high and uneconomic as the heat transfer and the productivity will be very low. However, with a ratio of 4, sulphur contents of 0.012-0.015% can be attained with 10% slag with one flush-off but with a ratio of 2.5 and 10% slag it would need three flush-offs as shown by the dotted lines in Fig. 9.16.

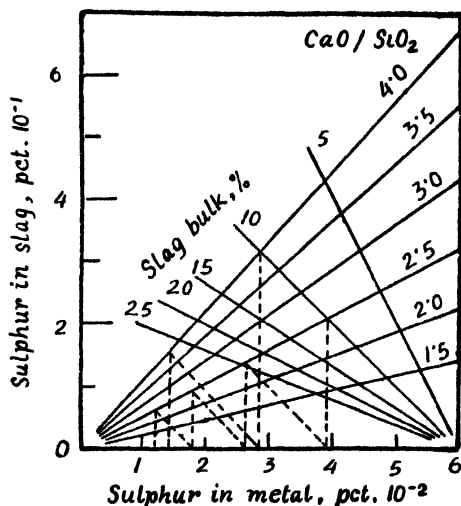


Fig. 9.16—Sulphur contents of slag & metal with 0.06% sulphur in the system at various lime-silica ratio with varying slag bulk.

Sulphur removal in practice⁵

The oxidising conditions prevailing in the open-hearth and the sulphur pick-up from the fuels used for firing are not conducive to any substantial desulphurisation of the metal. It is indeed difficult to make steel with lower sulphur contents than originally present in the pig-iron and scrap. The following measures may be helpful to keep the sulphur in steel under control :

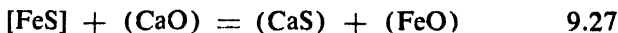
- (1) A considerable sulphur pick-up occurs during the melt-down period when the scrap is exposed bare to the furnace gases. Oxidising conditions during this period, an early slag acting as a protection and a shortening of the melting time, all hinder a sulphur pick-up. The pick-up is aided by low acid contents in the slag, reducing flame, a high temperature and a high sulphur in the fuel.
- (2) A high temperature helps sulphur removal.
- (3) A fluid slag induces sulphur diffusion and accelerates its removal. Fluor-spar and high temperatures increase the fluidity.
- (4) A larger slag-metal contact surface increases the reaction area and the diffusion and, thereby, accelerates sulphur transference to the slag. Turbulence caused by the 'boil' is therefore helpful.
- (5) A vigorous carbon boil may have a reducing effect on the (FeO)-slag and, therefore, influence the equilibrium position in favour of sulphur removal.
- (6) Sulphur removal is not enhanced by feeding MgO (as dolomite), contrary to the belief still held by many.
- (7) Desulphurisation is favoured by manganese addition.
- (8) Deoxidation in the furnace by ferro-silicon needs care and attention. Silica, formed from the oxidation of silicon, reduces slag basicity and induces a resulphurisation. On the other hand, silicon reacts with (FeO) and reduces the oxygen activity of the slag and metal and, thereby, helps sulphur elimination. Therefore, de- or re-sulphurisation depends upon the basicity and oxygen potential of the slag.

Since silico-manganese is a more efficient deoxidiser than silicon alone, the combined actions of the elements furnish less silica but cause substantial reducing action and help the removal of sulphur.

Thomas Process

There is no reason why the physico-chemical processes of desulphurisation in the basic converter should be any different from those in the basic open-hearth. Therefore, the basicity and the fluidity of the slag should be the primary factors governing sulphur removal. However, there has been diverse opinion regarding the state of combination of sulphur in the Thomas slag. It has been found by Oelsen³⁶⁻³⁸ that, in the immiscibility range of the system $\text{CaO-P}_2\text{O}_5\text{-FeO}$, the sulphur mostly remains in the FeO-rich layer and the sulphur in the phosphate layer is much less, even lower than in the iron melt. This has been corroborated by vom Ende and Mahn³⁹ in their experiments with Thomas slags. They have concluded from the activity calculations of lime in both the separated layers that, at least in the FeO-rich layer, the sulphur exists as FeS and not as CaS. This is also understandable since CaO in the FeO-layer is much less than in the phosphate-layer. The probability of the formation of FeS as a stable compound in the slag would suggest that FeO should be aiding the removal of sulphur. Peter, Esche and Oelsen³⁸ have found a favourable effect of (Fe)-slag on the sulphur ratio in their experiments in the silica-free lime-crucibles containing P_2O_5 . However, they did not find any such favourable effect of (Fe) in the Thomas converter, as was found by Wampach and Decker.⁴⁰ Weber and Kootz⁴¹ also found higher sulphur ratios with increasing (FeO). This may be attributed to the increased fluxing of lime by FeO.

The investigations on the influence of (FeO) have been stimulated by the assumption that desulphurisation proceeds according to :



It has been stated in the case of open-hearth that FeO acts favourably as long as the slag remains unsaturated with lime. Once the saturation is reached, a further increase in slag iron leads to a resulphurisation. This explanation should be valid for the principles of sulphur removal in the Thomas process as well.

Speith *et al*⁴² have shown from actual works data that there exists a close relation between (Fe) and basicity ($\text{CaO}+\text{MnO}$)

$/(SiO_2 + P_2O_5)$. The basicity increases from 1.83 at 7% FeO to 2.3 at 23% FeO. Whether the above is an equilibrium relation, could not be ascertained since both FeO and basicity increase with the time of blow. Since they both increase simultaneously in the slag and the lime is an extremely strong desulphurising agent, investigations have been made for finding the influence of FeO on desulphurisation, keeping the basicity constant. Speith *et al* found from their works data that, at constant (FeO), the sulphur ratio increased with the basicity. A compilation of the data enabled them to get a figure relating the sulphur ratio with the basicity for 4 different ranges of (FeO) and this figure resembled Fig. 9.3, except that only below the basicity of 2.4 the favourable effect of (FeO) was not discernible.

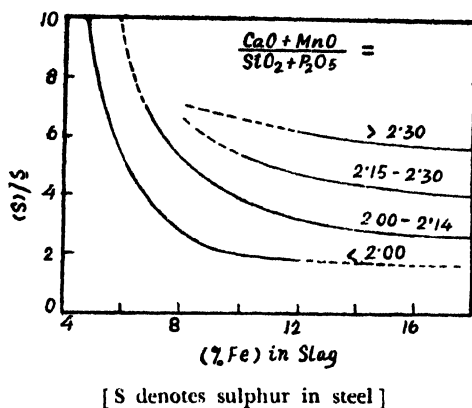


Fig. 9.17—Influence of iron content of Thomas slag at various basicities on sulphur distribution ratio. (K. C. Speith, H. v. Ende & H. Vosskoetter, Stahl und Eisen, 78, 1958, 155).

Fig. 9.17⁴² has been drawn with the sulphur ratio and (Fe) as co-ordinates for different basicity groups. The ratio decreases with increasing (Fe), the effect being much stronger at low basicity and (Fe)-contents lower than about 10%.

It has been observed that, in the Thomas process, the real desulphurisation starts only after the 'transition'. Sulphur removal increases when blown with oxygen-enriched air or with oxygen. From Fig. 9.17 and also from the fact that CaO is more stable than CaS, it is to be assumed that only a reducing condition would favour sulphur removal. In the Thomas process, such a

reducing condition is manifested at and just after the transition and the oxygen content of the metal falls rapidly during this short period (*cf.* Fig. 8.3). This might explain the sulphur removal after transition in the normal Thomas process but, in the case of oxygenenriched air, it can only be due to the early liquefaction of lime and the realisation of an early basic slag.

The influence of free-lime on sulphur removal has been investigated. Free lime is calculated by subtracting the lime used up in the formation of triphosphate and orthosilicate from the total lime. The sulphur ratio increases with free lime as in the open-hearth (*cf.* Fig. 9.19). The betterment of the ratio by free lime is, possibly, adversely affected by high (Fe), for the free lime is diminished by the formation of calcium ferrite. It is natural that SiO_2 would also adversely affect sulphur removal, since its increasing content reduces the 'free' lime.

The extent of desulphurisation in the Thomas process is 40-50%. The reason for higher values in other pneumatic processes will be apparent from the following section.

Gaseous Desulphurisation

Oxygen Processes⁵¹

Hitherto we have considered the influence of temperature, basicity and ferrous oxide of the slag on sulphur removal. Whereas in the open-hearth only 30-40% of sulphur is removed, in the Thomas process it is 40-50%, while in the oxygen processes the range is about 60-80%. An extensive desulphurisation could be achieved in the latter processes although the high iron oxide content of the slag should impair it. There have been indications^{15,25,43-52} in the last decade that not all the sulphur is held in the slag, but a part escapes in the gaseous form as SO_2 or SO_3 . Neuhaus⁵³ indicates that the use of oxygen jet on or in the slag in basic open-hearth has resulted in a desulphurisation of 50-70%, as against the normal of 30-40%, although in the former case the sulphur ratio $(\text{S})/[\text{S}]$ was less. Sulphur removal is more active when the bath carbon is low and the slag iron high. This, and other similar indications from various workers, can only mean an escape of sulphur from the slag through oxidation, the probable mechanism being:⁵¹



The oxygen-pressure of the slag in equilibrium with the open-hearth metal is of the order 10^{-8} - 10^{-12} atm.; whereas, a sulphate formation needs an oxygen-pressure greater than 10^{-4} - 10^{-6} atm.^{7,8} According to Speith *et al.*¹³ the sulphate formation increases, the higher the temperature and lower the $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio in the slag. In the open-hearth, the sulphur in the slag is present mostly as sulphide. But it is possible for sulphur to exist as a sulphate if the gaseous phase is highly oxidising and the metal-slag and gas-slag interfaces are not in equilibrium, as can happen with viscous, foaming and non-turbulent slags. Fig. 9.18⁵¹ shows that even with a low oxygen potential in the gas phase, it is possible to obtain a desulphurisation of the slag, although the rate is small. The velocity may go up to 1% (S)/min even with an oxygen partial pressure of 10^{-4} - 10^{-6} atm.

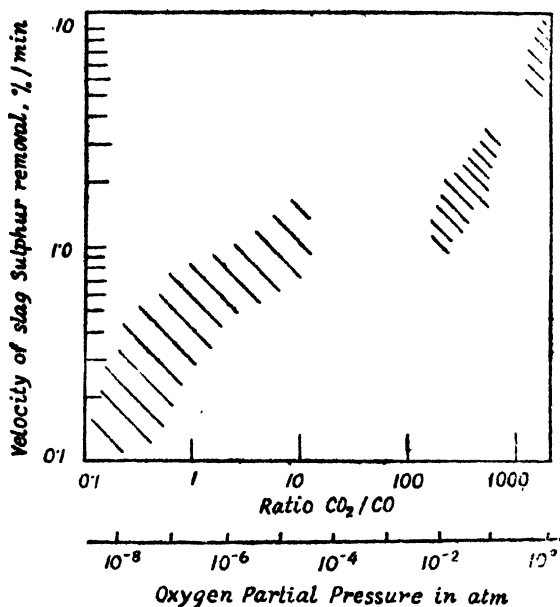


Fig. 9.18—Relation between oxygen potential of gas phase and the rate of desulphurisation of slag. (H. Neuhaus, H. J. Langhammer, H. Kosmider & H. Schenck, *Stahl und Eisen*, 82, 1962, 1279).

The extent of desulphurisation in the oxygen processes is dependent upon the oxygen pressure of the gas phase in contact with

the slag (apart from the influence of the basicity and the slag volume which is common to all basic processes) and generally ranges from 30 to 50% (in basic open-hearth, it is on the lower side since the fuel sulphur takes part in the reactions).

In the laboratory experiments, Neuhaus *et al.*⁵² have found that 80-90% sulphur could be removed from the metal and 50-60% of the total sulphur escapes in the gas phase. A desulphurisation of 60-80% (20-45% of total sulphur going away in the gas) has been observed in the Kaldo (with Thomas pig), Rotor, Elliptical, Buffer slag, LD-AC and OLP processes. In these processes, the refining is carried out indirectly by the slag and the oxygen jet impinges on or in the slag layer. The comparatively slow decarburisation keeps the oxygen potential of the gas phase high and thus a considerable build-up of ferric oxide is possible. The distance of the equilibrium between the slag and the metal is also greater. In the buffer slag process, the sulphur ratio is only 1-3 but, due to a large escape of the element in the gas, $[S] \sim 0.005\%$ may be reached. During 'fine dephosphorisation' in the Thomas process, there is a little ferric oxide build-up in the slag with the consequent slightly higher sulphur removal (50-55%) than in the normal process. The iron content is higher ($\sim 25\%$) in the second slag but the free lime is also greater.

The duration of the oxygen blow and the slag bulk have also a considerable influence. Gaseous desulphurisation is, generally, greater if the refining time is longer and the slag bulk higher.

In the Thomas and LD and Kaldo (using open-hearth pig) processes, the gaseous desulphurisation is rather low. In the Thomas process, the oxygen partial pressure in the waste gases is small and the slag-metal reactions approach equilibrium due to turbulence. In the LD process, the oxygen jet impinges on the metal surface and the refining is more or less direct. The initial sulphur and the slag volume are also small. The latter two factors in the Kaldo (open-hearth pig) inhibit sulphur removal in the gases.

Basic open-hearth

Normally, the extent of sulphur removal is 30-40% but, with the oxygen lancing it is possible to reach even 60-70%. This is possible because of gaseous desulphurisation, although the sulphur ratio in the oxygen-blown heat is lower than in the normal.

This is clear from Fig. 9.19⁵¹ where the free lime is drawn against the sulphur ratio on the one hand and per cent desulphurisation on the other, for both the cases. It is to be noted that per cent desulphurisation in the case of oxygen lancing decreases with increasing free lime, above about 20-22%.

Neuhaus *et al.*⁵¹ draw the following conclusions regarding desulphurisation in the basic open-hearth :

- (a) Metal-slag desulphurisation is favoured by : increasing basicity and decreasing oxygen potential of the slag, increasing temperature, greater turbulence and larger metal-slag interfacial area.
- (b) Gas-slag desulphurisation is favoured by : increasing oxygen potential of the slag and gas phases, decreasing slag basicity, increasing temperature and larger gas-slag interfacial area.

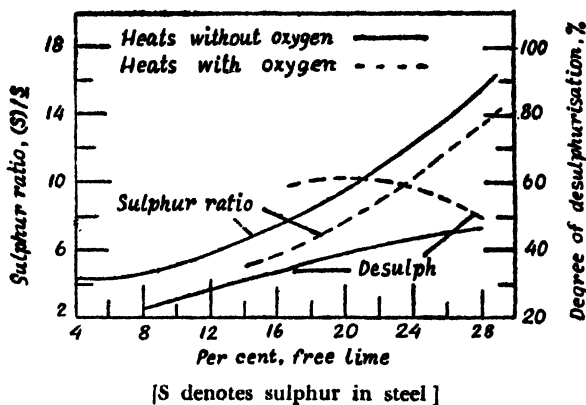


Fig. 9.19—Influence of free lime on sulphur ratio and per cent desulphurisation in basic openhearth melts with & without use of oxygen lance. (H. Neuhaus, H. J. Langhammer, H. Kosmider & H. Schenck, *Stahl und Eisen*, 82, 1962, 1285).

Sulphur removal in the basic electric furnace⁶⁰

We have seen on pp. 316-22 that sulphur removal is facilitated by a high slag basicity and a low iron-oxide content of the slag. The temperature plays a part, in so far as a highly basic slag is obtainable in a fluid state at high temperatures. A necessary physical condition for desulphurisation is the area of slag/metal contact surface. Therefore, a turbulence in the bath is helpful in that

it increases the contact surface as well as the diffusion of sulphur to the interface.

In the open-hearth, where the conditions are oxidising, the sulphur distribution ratio is very low, 2-10; (FeO), above 3%, does not seem to affect the ratio. With reducing slags containing FeO less than 3%, the conditions are very different. In the blast furnace, the ratio varies between 50-350. Although the sulphur ratio is a function of the so-called *excess base* and the blast furnace slag contains much smaller excess base than in the open-hearth, yet the desulphurisation is several times higher in the former. Sulphur distribution ratio increases enormously as FeO in the slag falls below 1%. Such extreme reducing conditions are available in the basic electric furnace slags. From Fig. 9.5, the sulphur ratio is very high at low FeO and falls sharply as the FeO increases. This can be explained by assuming the sulphur reaction to follow Eqs. 9.2 and 9.25.

Apart from the beneficial effect of lime, the desulphurising action of reducing slags is due to the transference of [O] to the slag as (FeO). As (FeO) is reduced, the slag takes up more oxygen from the metal, thereby accelerating the forward reaction of the above equations.

Mowat,⁵⁴ in his experiments on the production of rimming steels in the electric arc furnace with single oxidising slags, has shown that a ratio of 15-20 can be obtained even with (Fe) as high as 20%. This he attributes to the possibility of working with very limy slags (excess base of 0.40-0.55), because of the high temperatures reached in such furnaces. Temperature itself, he agrees, has no effect on desulphurisation but high temperatures enable melting out with a highly basic slag. In fact, a higher sulphur ratio than corresponding to equilibrium was found while working under such slags. In the basic open-hearth, one has to work with much lower basicity, in the range of -0.05 to + 0.35. It is difficult to keep more basic slags in a fluid state under the open-hearth conditions.

Highly basic and reducing slags are important for sulphur removal, but the diffusion of sulphur from the metal to the metal/slag interface is of no less importance. The stirring action of the bath and slag in the open-hearth is performed by the carbon boil, which lacks in the electric arc furnaces, especially in the reducing

period. Here, the diffusion is only possible due to the convection current inside the bath caused by heat. This process, being naturally slow, retards sulphur removal and prolongs the heat with the consequent loss of time, increased erosion of refractories, etc. Nowadays, inductive stirrers are used for the creation of a turbulence and this accelerates desulphurisation during the reducing period when the boil is absent.⁵⁵ The stirring action also helps in the equalisation of the metal temperature and speeds up deoxidation, which takes place through the diffusion of oxygen from metal to slag (*cf.* Chap. XI). A stirring action can also be achieved by bubbling inactive gases like argon through the metal, which also helps in the 'washing away' of some hydrogen.⁵⁶

A considerable desulphurisation can also be effected by injecting fine calcium carbide inside the molten metal with the help of argon, CO_2 or nitrogen at high pressures. Carter⁵⁷ has shown that sulphur in the metal (0.04-0.05%) can be reduced by 50% by this method. The disadvantage of this method is the pick up of carbon from CaC_2 .

Besides injecting CaC_2 , other chemicals and alloys in the powdered form like burnt lime, calcium cyanamide and silicide, Ca-Si-Mn, Ca-Si-Mg, etc. can also be used.⁵⁸

Stainless steel from scrap in the molten state can be desulphurised in the same manner. After obtaining a good heat with the temperature of $\sim 1,560^\circ\text{C}$ and making a liquid basic slag with lime and fluorspar, the carbide is injected in the metal through the slag layer by introducing a steel tube and blowing 50-100 lbs. of carbide (for 3 ton furnace) in powdered form by nitrogen. Depending upon the amount of initial sulphur, the nature of slag and the amount of CaC_2 injected, a 50% reduction of sulphur can be easily effected.⁵⁹ The carbon picked up is subsequently oxidised, by an oxygen jet, to about 0.03%.

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CHAPTER X

THE RESIDUAL OXYGEN IN STEEL

General

Steelmaking processes are mostly carried out by oxidation. It is natural, therefore, that steel should pick up oxygen. Its content at the end of the processes depends not only upon the metal and slag compositions and the temperature but to a great extent also upon the variations of the processes themselves. The *residual* or *end*-oxygen content is of importance not only for killed steels but also for the semi-killed and rimming varieties. The residual oxygen in steel is directly related to its mechanical properties as well as to proper casting and shaping of ingots. It is, however, difficult, rather it is impossible, to find the oxygen content by analysis in view of the short time interval between tapping and teeming of the molten steel. An effective deoxidation can only be carried out during this period. It is the purpose of this chapter to study the end-oxygen contents of steel in different steelmaking processes and the influence of the variations of these processes on the end-oxygen.

Oxygen is present in steel either in the elemental form or as FeO. It is possible, theoretically, that the oxygen may be present as any other oxide the metal comes into contact with e.g. SiO₂, MnO, CaO, Al₂O₃, MgO, etc. but their solubilities in steel are so insignificant that such assumptions have been finally discarded. What is more important as far as such oxides are concerned, that these may be, singly or together, present as non metallic inclusion being unable to separate out due to various reasons.

The solubility of oxygen in liquid iron increases with the temperature (*cf.* Eq. 3.6). Its amount depends upon the iron oxide activity or the free FeO-content of the slag in contact, and in equilibrium with pure liquid iron. In practice, the metal contains other elements whose presence affects these values. Manganese does not seem to possess any influence. But carbon, as long as it is present in a sufficient amount, exhibits a decisive influence on the residual oxygen in steel. As we know, the C-O reaction is governed by the equilibrium relation—%[C]. %[O] = 0.0025. This value is

generally accepted to be valid at steel-making temperatures, although the constant is a function of the temperature as well as the [C]-content. In actual steelmaking, however, equilibrium between these two elements is seldom reached (except in certain special circumstances to be seen later, or when the [C]-content is below 0.05%—in which case the [O]-content is largely determined by the FeO-activity of slag) because of the restrictive factor of the nucleation of CO bubbles.

The end-oxygen in soft steels, produced in the basic open-hearth and electric furnaces, depends largely upon the slag composition; whereas, for the harder varieties, it depends on the carbon content to a large extent. The extent of approach towards the equilibrium is dependent upon the rate of the 'boil' and the supply of nuclei e.g. gaseous oxygen (in case of oxygen lancing) and/or furnace additions. In the acid open-hearth, the viscosity of the slag is a further restrictive factor. Modern oxygen-blowing processes producing carbon-steels follow the same basic pattern as in the open-hearth or the electric furnaces.

In the Thomas process, the carbon is almost completely eliminated before the final dephosphorisation starts. Metal oxygen is controlled by the slag composition.

In the acid Bessemer process, the oxygen content during the initial blow, and after, is largely determined by the [C]-content. Below a carbon concentration of about 0.1%, the oxygen in steel rises steeply due to the rapid burning of iron into its oxides. The effective control of [O] depends upon stopping the blow at the proper moment, which comes only from experience.

Basic Open-hearth

In basic open-hearth steelmaking, as in most other steelmaking processes, the tapping oxygen value depends upon the slag and metal compositions as well as on the method of refining. However, carbon possesses the dominant influence and determines the end-oxygen content although an equilibrium is not established between them.

In Chapter V we have mentioned that in the open-hearth processes, the actual oxygen lies somewhat above the equilibrium [O] by an amount $\Delta[\text{O}]$ which does not depend upon the temperature and [C] but on the state of boil and hearth refractories. The

value lies somewhere intermediate between the oxygen in equilibrium with the carbon in the metal and that in equilibrium with the slag. Only below about 0.1% [C], does the [O] approach the value corresponding to a_{FeO} of the slag. Larsen¹ also has found that $\Delta[\text{O}]$ is more or less a constant quantity during a steady or an undisturbed boil, above 0.1% [C]. $\Delta[\text{O}]$ under these conditions varies from 0.015-0.025%. The slag viscosity, basicity, (MnO) and [Mn], temperature of the metal, do not appear to possess any influence on the steady state value of $\Delta[\text{O}]$.

Fetters and Chipman² gathered from a mass of open-hearth data that the [C]-[O] product varied from heat to heat and to a greater extent from plant to plant. But a guess can be made of the value of [O] from an analytical [C]-content, during a steady state heat, from the average value of the product :

$$\%[\text{C}] \cdot \%[\text{O}] = 0.0028 + 0.011\%[\text{C}]$$

Fig. 5.1*b*. shows the great dependence of [O] on the [C]-content in the open-hearth. During refining, the [O]-content increases as the [C] decreases. But all along, [O] lies above the equilibrium curve based on Vacher and Hamilton's value³ of [C] · [O] = 0.0025. Even if the carbon and oxygen could attain equilibrium in the open-hearth, it is necessary for the bath to contain an excess of oxygen, for otherwise no carbon reaction can take place. Any reaction can only occur when the concentrations of the reactants are higher than the equilibrium values. The required excess oxygen is supplied continually by the heating gases through the slag or by the ore or millscale additions used to maintain the carbon reaction. The reaction may stop either when the carbon has decreased enormously or when the supply of oxygen from the slag is restricted.

There can be no doubt that decarburisation is stimulated by bubble formation. Theoretically, therefore, the carbon reaction cannot obey the LMA. Schenck,⁴ however, has used the LMA (cf. Eq. 5.8) as a basis for studying the carbon reaction and investigating the influence of various other factors. The rate of decarburisation is a factor of temperature, oxygen potential of slag and carbon content of metal. These in their turn determine the [C]-content of metal, since the latter is dependent on the two opposing reactions : one being the velocity of diffusion of oxygen

to the metal and the other, the consumption of oxygen by the carbon reaction $[O] + [C] = CO$. The $[O]$ -content could possibly correspond to the equilibrium value, and therefore be minimum, only when the carbon reaction has stopped and the boil subsided. The analytically determined $[O]$ in the open-hearth, which lies much above that given by $[C]/[O]$ equilibrium, is determined largely by the iron-oxide activity, composition and fluidity of the slag, temperature and the total area of bubble surface (*cf.* Chap. 5). Since Schenck has formulated the decarburisation equation from the study of a mass of steelmaking data, all the factors affecting the reaction velocity are included in the mass law constants and it is possible to find the actual $[O]$ from his equation.

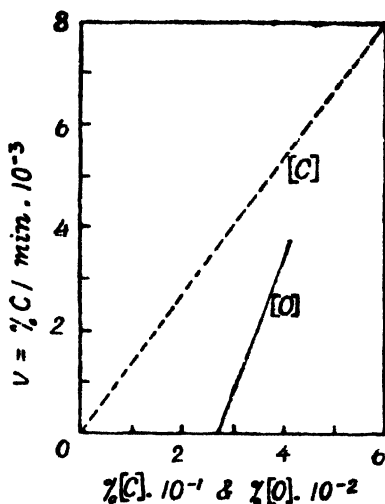
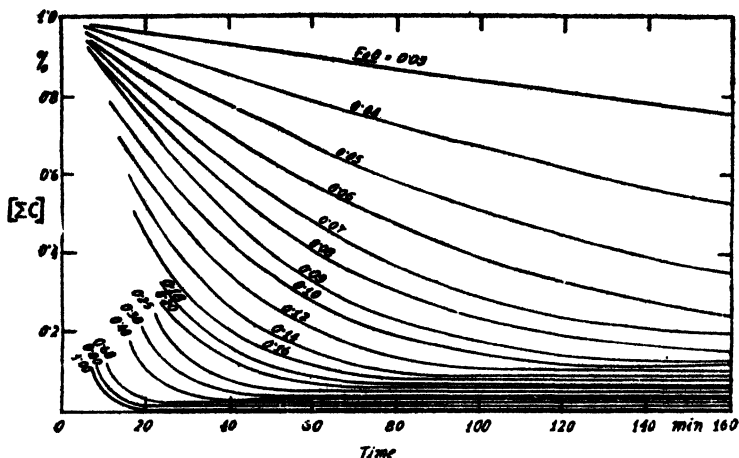


Fig. 10.1—Dependence of rate of decarburisation on oxygen & carbon contents of steel. See text also. (K. G. Speith & H. V. Ende, *Stahl und Eisen*, 74, 1954, 517).

Since k_1 and k_2 of Eq. 5.8 do not vary much within a small $[C]$ -concentration range, the rate of decarburisation should be a linear function (if the equation is valid for open-hearths), of $[C]$ and $[O]$ when either of them is kept constant. This is confirmed in Fig. 10.1⁵ where v is plotted against $[O]$ for $[C] = 0.10 \pm 0.01\%$ and against $[C]$ for $[O] = 0.02 \pm 0.005\%$. The analytical values of $[O]$ and $[C]$ fall approximately on the calculated

lines shown in the figure. It is important to note here that the equation is valid for an *undisturbed* boil, in the absence of fresh additions.



[FeO denotes iron oxide contents of steel]

Fig. 10.2—Graphical determination of ferrous oxide dissolved in steel in acid & basic openhearth from time-concentration curve of carbon. (By permission from 'The Physical Chemistry of Steelmaking' by H. Schenck).

From Eq. 5.8 it is possible to estimate $[\text{FeO}]$ or $[\text{O}]$ in steel if the rate of decarburisation is determined k_1 , k_2 and r_{CO} are obtainable from Schenck's work. v can be determined from a plot of carbon drop with time. From the so obtained plot, v at any $[\text{C}]$ is found out from a tangent at that point. In order that the equation may be gainfully employed for at least a rough estimate of $[\text{FeO}]$ (and, therefore, $[\text{O}]$), Schenck has produced a diagram from where the steel oxygen can be directly read, while the liquid metal is still in the furnace. Fig. 10.2⁴ has been drawn with $[\text{C}]$ and time in minutes as coordinates. $[\text{FeO}]$ -value for each curve is also given in the figure. There exists a definite refining curve of carbon for any given $[\text{O}]$ or $[\text{FeO}]$ since, from Eq. 5.8, the latter determines the refining rate for each carbon content. This rate falls with decreasing $[\text{C}]$. It can be seen from the diagram that if the course of refining follows the 4th curve from the top, the steel contains 0.06% $[\text{FeO}]$ or 0.013% $[\text{O}]$. In practice, however, the oxygen content is not uniform throughout a heat and

the refining curve will not follow any particular [FeO] line but rather run successively parallel to the various [FeO] lines. The oxygen content will be given by any curve of the diagram which corresponds at any instant, in slope and in carbon content, with the actual operational works refining curve.

For rapid and practical use of the diagram it is necessary to prepare a standard transparent positive of Fig. 10.2 whose scales of axes must be identical with those in the routine works refining curves. Schenck recommends the scale $0.1\% [C] = 10 \text{ mm}$ and $10 \text{ minutes} = 10 \text{ mm}$ to be convenient in works practice. The change of [FeO] with time and carbon content during the entire refining period can be ascertained by systematically sliding the transparent positive horizontally over the works curve as drawn, so as to find the common slope for the corresponding carbon contents.

Whatever may be the theoretical controversies regarding the mechanism of carbon reaction in the open-hearth, the fact remains that the oxygen content of steel can be estimated to an error of only $\pm 0.002\%$ during refining, provided [C] and v at any moment are known with sufficient accuracy. Mackenzie,⁶ Speith and Vom Ende,⁹ Hess⁷ and Krabiell⁸ have all come to the conclusion that the oxygen in steel can be correctly estimated (corresponding to analytical values) by the graphical method of Schenck. It may, however, be noted that [O] so determined is present as reactive dissolved oxygen or [FeO] and not as oxides such as non-metallic inclusions.

The relationship between v and [O] shows that the [O] is greater, the higher the rate of decarburisation. This is amply borne out by Fig. 10.3a⁹ where the [O]-content increases with v for [C] contents lower than $\sim 0.15\%$. With the rising rate of decarburisation, the [O]-content deviates farther and farther away from the equilibrium value which for $0.1\% [C]$ is $0.025\% [O]$ and for $0.15\% [C]$ is $0.016\% [O]$. But, at higher [C] concentrations, the [O]-values are no longer functions of v because the deoxidising power of carbon at such high concentrations determines the ultimate [O]-content and outweighs all other influences that affect the oxygen-contents. Apart from the above reason, there may be others the nature of which are still unknown. Schenck¹⁰ also agrees that, above about $0.4\% [C]$, his equation

frequently fails and the analytical values of oxygen do not correspond with those determined by the graphical method.

At low $[C]$ -contents ($<0.11\%$), the iron content (ΣFe) of slag has a profound influence on $[O]$ as can be seen from Fig. 10.3*b*. This is caused by the higher oxidising power of the slag and the simultaneous decrease of $[C]$ with increasing (ΣFe).

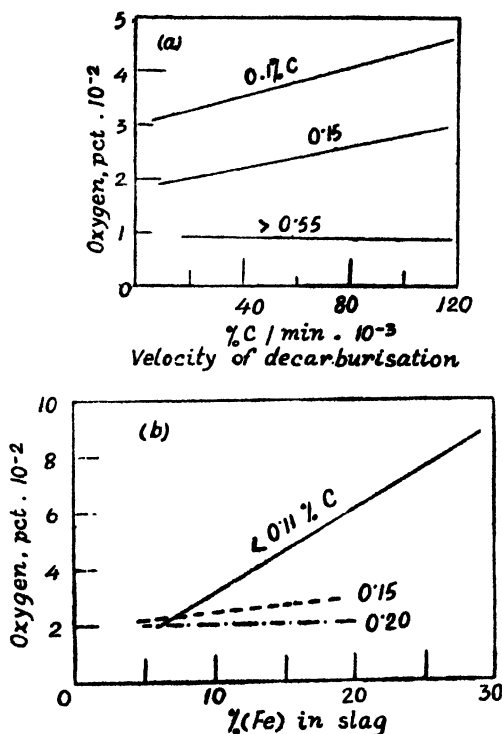


Fig. 10.3—(a) Influence of decarburisation rate on oxygen in steel in open-hearth at different carbon contents.

(b) Influence of iron in slag on oxygen in steel in openhearth at different carbon contents. (K. G. Speith & H. v. Ende, *Stahl und Eisen*, 76, 1956, 1164).

At higher $[C]$, such influence is much reduced and, at 0.2% $[C]$, the $[O]$ content is not affected by (ΣFe) for all practical purposes. We can conclude that for basic open-hearths, (ΣFe) has practically no influence on $[O]$ and between, say, 0.2 – 0.4% $[C]$ the $[O]$ -content is determined alone by the decarburisation rate.

It must be emphasised here again that Schenck's graphical method of determining oxygen during refining is applicable provided the refining proceeds *undisturbed*. Any change in the conditions during the period may give higher or lower analytical values than corresponding to Schenck's equation. Hess⁷ in his recent extensive investigations on basic open-hearth furnaces, for finding the effect of various additions, action of flame, etc., in order to establish conditions for obtaining uniform tapping carbon and oxygen contents, has reached the following conclusions :

- (1) The analytical values of oxygen correspond to the calculated ones (by Schenck's method) during an undisturbed refining, the heating being normal and with uniform flame.
- (2) The same applies when lime dissolves in the slag or pig-iron is added to the bath for deoxidation.
- (3) If the heating flame is reduced, the refining rate becomes slower without any corresponding lowering of the oxygen content. Afterwards the refining regains its normality gradually.
- (4) Additions of ore or flux boost the refining and lead the [O]-contents to lower values than the calculated ones.
- (5) On addition of ferro-manganese to the bath, the refining follows Schenck's equation if such an addition slows down the oxygen transfer ($\text{FeO} \rightarrow [\text{O}]$). If, on the other hand, the used-up [O] is readily replaced by the slag oxygen, the refining may be boosted up as with the additions of ore or flux.

In order to obtain uniform values of [C] and [O] at the tapping of rimming soft steels, Hess⁷ suggests the following :

- (1) The slag, up to the time of tapping, must be kept reactive enough so that it can deliver oxygen to the bath for an unrestricted refining. Such additions and slowing down of heating as would increase the slag viscosity should be avoided in the later phase of refining. These would help in a uniform refining; therefore, a uniform quality of steel can be obtained.
- (2) If a boosting of the refining rate is necessary just before

the tapping, it should be done by adding flux or ferro-manganese. Ore at this stage should be avoided.

- (3) The quantity of slag has some influence on refining, especially when the temperature increases considerably. The greater the hearth area and the amount of slag, the greater is the refining rate.

For obtaining a good quality steel, the oxygen in steel should generally be low (except in the case of rimming steel).

A low-[O] steel can be obtained by a proper adjustment of slag and refining rate. Further, a knowledge of the tapping oxygen is helpful for a judicious use of the deoxidisers. It is possible to ascertain [O] with a high degree of certainty by Schenck's graphical method if adequate precautions are taken to record the carbon refining curves. It is well-known to steelworkers that a high refining rate before tapping is injurious to the steel quality. Again, a low initial refining rate leads to a poor quality, although, in view of the relation between v and [O], a low rate requires less of oxygen. It must not be forgotten that a vigorous boil and mechanical agitation are necessary not only for the removal of the gases (hydrogen and nitrogen) and driving away of the slag inclusions, but an excessive initial oxidation (which causes the vigorous boil) is a primary factor for obtaining a clean steel.²⁰ It is possible that the scrap and pig-iron may contain Al and Si which, in the absence of sufficient oxygen, form solid alumina and silica. The scrap itself may contain initially considerable amounts of alumina and silica. Such solid suspensions will liquefy and rise to the top and be incorporated in the slag, as seen from Fig. 11.3, only when a large amount of oxygen is present; and the lower the [Mn], the greater is the need of oxygen supply. For the same reason, in electric arc-furnaces, the steel quality sometimes is inferior to that expected. Here, the melter strives to maintain a reducing atmosphere which is not enough to prevent the oxidation of Al and Si into solid suspensions, whereas the oxygen supply is insufficient for the liquefaction of those suspensions; these suspensions may not be able to separate out from the bath during the refining period and would remain entrapped during casting. Therefore, it is not at all advantageous in the open-hearth or electric steelmaking to

restrict the supply of oxygen, at least during the initial refining period. On the other hand, it is useful and necessary to deliver a large amount of oxygen, for removing the oxide suspensions, which is accompanied by a vigorous carbon reaction with the advantages of mechanical removal of the gases and suspensions (they adhere to the CO-bubbles and rise up).

It may be noted here that carbon decreases the activity of oxygen in iron. Therefore, at higher [C]-contents, the [O]-contents necessary will be correspondingly more for the liquefaction of the suspensions, as has been made clear by the curves *Ia* and *IIIa* (Fig. 11.3) which are valid for 0.5% [C] melts.

From what has been said above, it is necessary to have an ample decarburisation (or ample supply of oxygen) at the beginning of refining for cleaning the steel. But this initial excessive oxidation has to be compensated for by decreasing the refining rate in the later period before tapping. Beitter¹¹ suggests that the refining rate must be such as to give a straight line carbon refining curve so that, at the end, a rate of 0.0037% C/min. may be obtained in the case of basic open-hearth Cr-Ni steel making. It has been often experienced that a high initial oxidation produces poor steel. This can only be perhaps because suitable slag control measures have not been taken early so as to retard the carbon reaction in time and arrive at the desired final [C] level sufficiently slowly. The suggestion that highly oxidised rusty scrap leads to a steel with high final oxygen cannot be entertained for the same reasons. With proper control of the refining rate, there is no reason why the steel should be dirty with a high initial iron oxide content. Rather, the rusty scrap should help in the liquefaction of the solid suspensions like alumina and silica as well as in the driving off (because of a vigorous boil) of the gases which usually accompany the impure scrap in considerable amounts.

As regards the measures by which the refining rate can be slowed down, it can be achieved by adding lime to the slag and decreasing the flame (by reducing the air used for burning the fuel). Both these measures reduce the slag temperature, increase the slag viscosity and reduce the oxygen potential of the slag. As has been explained earlier (cf. Fig. 4.5), in the range of basic steelmaking slags, an increase of lime decreases the iron oxide

activity. If, at first, the refining rate has slowed down considerably, it is possible to regenerate it later by additions of pig iron and ore and maintain a steady slow boil. This process is, however, uneconomical and the fresh additions are likely to bring in further suspensions which may not separate out during the available time.

It is not possible to suggest any particular refining curve or the final oxygen-contents to be aimed at for the innumerable grades of steel. Every plant and every open-hearth furnace must have its own refining curve for any particular variety of steel. Further, the value of $[O]$ as given by Schenck's transparency method is valid at a given time only, depending on the prevailing $[C]$ and the instantaneous rate of refining and not on the overall rate. Thus, the mean rate of decarburisation possesses only a qualitative value which is, however, useful if the making of any particular grade of steel is standardised in any particular furnace.

Again, a knowledge of only the final $[O]$ -content may not be very useful if consideration is not made about the absorption of oxygen from the atmosphere during tapping and teeming, the slag-metal reactions in the ladle, the amount of deoxidisers used and the method of deoxidation. Once all these factors are taken into account and they are kept relatively constant, it is possible to make at least a qualitative use of $[O]$, determined from the refining curves. The author recommends that the refining curves be made for each variety of steel by statistical analysis of the rolling mill rejects. Keeping all other variables constant, the particular $[O]$ which gives the lowest rejects should be aimed at, by suitable adjustments of the refining rate, with the help of Schenck's method.

Acid Open-hearth

The principle of the oxidation of carbon in the acid open-hearth is the same as in its basic counterpart. Schenck's equation is valid for both the processes. There is no reason why the graphical method of determining $[O]$ or $[FeO]$ should not be applicable to the acid process. In fact, Fig. 10.2 is valid for acid as well as basic open-hearths. In the acid process, the final oxygen is much lower than in the basic one and the finished

product is much cleaner. In contrast to the manganese in the basic open-hearth, the silicon in the acid process has been erroneously considered as an index of steel quality. It is a fact that Si is much more deoxidising than Mn and a high [Si] in the metal is a sure sign of low oxygen in steel. But the [O]-content cannot be defined by Si alone, even if the temperature and the slag composition are fixed and whether the latter is saturated with silica or not. The presence of MnO , Al_2O_3 , CaO , in the slag or Mn in the metal has a profound influence on the equilibrium constant (Eq. 3.22) and they lower the K_{Si} considerably. Moreover, the bath invariably contains carbon which upsets all relations between [Si] and [O] (cf. Fig. 3.16). It is doubtful whether any slag-metal equilibrium is attained at all in the acid open-hearth. We have already discussed on p. 50 that the reduction of Si and Mn from the slag to the metal is a factor of the slag viscosity. A viscous slag hinders the transfer of slag-oxygen to the metal which induces carbon to reduce the silica of the hearth lining. The reduced silicon in the metal reacts with the oxygen diffusing from the slag and is oxidised to silica. It is incorporated in the slag which becomes more viscous and therefore encourages further reduction of Si to the metal. Thus the concentration of Si in the acid open-hearth metal depends upon the difference of the amount reduced, and that later oxidised, and in the absence of a slag-metal equilibrium a unique relation between oxygen and silicon cannot build up. It is true that the acid open-hearth steel is cleaner and contains lower final oxygen. This is not due to a high silicon in the metal. We should rather imagine that the reduction of Si from the hearth lining or the slag is facilitated due to an already low oxygen in steel, caused by the high slag viscosity and the carbon reaction.

The [O]-content of the acid open-hearth steel can be as low as 0.008%, depending upon the metal and slag compositions. From Fig. 10.2, the [O] can be quantitatively assessed, at least approximately, by Schenck's transparency method. As regards the intensity of refining, the same arguments hold good as in the basic process but the final refining rate in the acid process should be much slower. Beitter¹¹ suggests 0.0019% C/min. to be suitable for Ni-Cr steels. The variation of [O] in an actual heat is shown in Fig. 2.15.

Pneumatic Processes

Acid Bessemer : In the case of open-hearths the oxygen is supplied to the metal by the heating gases through the slag layer, whereas in the bottom-blown conventional converters the air directly oxidises the iron to ferrous oxide. The oxide or $[O]$ reacts with Si and Mn to form the respective oxides and the primary silicate solution thus formed incorporates FeO from the metal to make the acid slag— $FeO-MnO-SiO_2$. As the metalloids are progressively removed from the pig-iron, the oxygen potential of the metal increases continuously and the slag takes up more and more of iron oxide in order to attain an equilibrium with the metal. It is, however, doubtful if such an equilibrium is established at all since the oxygen is supplied to the metal at a very high rate. At any moment during the blow, the oxygen activity of the metal is greater than that of the slag. Therefore, any calculation of $[O]$ from the a_{FeO} of the slag will give a lower value.

In the acid bessemer system, the partition co-efficient $L = (FeO)/[O]$ is not applicable and the $[O]$ is much greater than given by the relation. This is because an acid bessemer usually uses iron with $Si/Mn = 2.2.5$ which furnishes a dry solid to viscous, partly semi-solid slag. This slag is relatively inert and there is but a little inter-action with the metal. As long as sufficient carbon is present, the state of metal oxidation is low and only when the carbon flame drops a rapid generation of FeO begins. This FeO is unable to give itself up to the dry slag and hence the large build-up of oxygen in the metal. Although this $[O]$ is much larger than it would be if allowed to interact with a liquid slag (since, due to the violent agitation, $[O]$ rapidly passes over to the liquid slag in the direction of equilibrium), yet during the subsequent deoxidising addition of ferro-manganese the loss of manganese is much lower. This, at the first sight, may seem paradoxical. In fact, however, manganese reacts in this case only with the metal- and not with the slag-oxygen. In the case of a liquid slag, although the metal oxygen is lower, the overall iron oxide content in the slag-metal system taking part in the reaction is much larger, with the consequent greater loss of manganese.¹² Any over-oxidation of the metal would lead to a fluxing of the dry slag by the excess of generated FeO, resulting in a greater

Mn-loss and erratic final analysis. A proper control of the blow and the end point should give uniform [O]-contents and lesser rejects or off-casts. The relation between oxygen and carbon during the blow is shown in Fig. 5.12.

Blowing of low-silicon/high-manganese pig iron results in a liquid acid slag. In such a case, any addition of ferro-manganese will entail large Mn-losses and, therefore, it is desirable to drain off the slag before such additions are made. Since the metal oxygen in contact with a liquid slag is less than that when in contact with a dry one, the production of rimming steels creates difficulties, as such steels need a higher metal oxidation. In these cases, after draining off the slag, the metal can be re-blown for a very short time so as to attain the required oxygen level.¹²

Thomas Process: Thomas steel, in comparison to acid bessemer, may be assumed to attain higher [O]-contents because in the latter process the dephosphorisation period with its requirement of high oxygen potential is omitted. As long as a sufficient amount of carbon is present, there is no reason to believe that the [O] will behave differently in the two processes. As the carbon is progressively removed, the [O] in steel increases correspondingly but not to any great extent since any FeO formed is immediately reduced by carbon. When the burning of carbon comes to an end, the [O]-content rises slowly and reaches 0.025-0.04%¹³⁻¹⁴ at the disappearance of the carbon flame. Afterwards, the [O] rises rapidly to 0.07-0.12%, depending upon the basicity and (Fe)-content of the slag, [P] and the temperature.

During the 'after blow' period, the phosphorus reaction becomes very active in the presence of a highly basic liquid slag. At this time the requirement of oxygen by the phosphorus is so great that, for a time, it withdraws more oxygen from the bath than is supplied by the air. The state of the bath and the slag becomes so reducing that even Mn is reduced back to the metal from the slag, resulting in the well-known *manganese hump*.

The range of the oxygen contents in the Thomas steel at the end of the process was found by Körber and Thanheiser¹⁵ to be 0.07—0.10%. According to Speith and vom Ende the values (before removing the slag or adding ferro-manganese) are func-

tions of the temperature and range from 0.04—0.08% at 1,560°C and from 0.07—0.12% at 1,700°C. These values are evidently much higher than the open-hearth steel containing about 0.1%C. They rise slowly upto about 1,650°C and then rather steeply and are valid for Thomas steels blown with air and oxygen enriched air (30%—O₂) in the bottom-blown converters as well as for the top blown steels (with 98%—O₂), the samples being analysed in all the three cases after the end of the carbon reaction. The comparatively wide range of the oxygen values denotes that apart from the temperature, they are also dependent on other factors. For example, the [O]-content rises with the increasing iron content of the slag. Independent of the methods employed, the temperature and the (Fe)-slag determine to a very large extent the [O]-contents in Thomas steel (after the removal of carbon). The iron content of Thomas slags, at the end of the carbon reaction, is generally below about 7% and starts rising only when the phosphorus content drops below about 0.1%. The effect of iron and the impurities in the slag as well as that of temperature on oxygen in steel will be clear from Figs. 3.30 and 8.12.b.

The [O]-content decreases with increasing basicity of the Thomas slag. This is understandable since, from Fig. 3.26, the a_{FeO} of the Thomas slag, for constant (FeO), decreases as the composition moves away from the miscibility gap and approaches the CaO-corner.

The relationship between the temperature, [O] and the [P] in Thomas steel has been described on p. 108. In contrast to open-hearth steel, the final [O]-content in Thomas steel is determined, not by carbon, but rather by phosphorus. In the open-hearth, the [O]-values lie above (and sometimes on) the [C]/[O] equilibrium isothermal values of Vacher and Hamilton, whereas in the Thomas steel the values are less than what one should expect from the [C].[O] product. However, the [O]-values in the Thomas process are larger than in the open-hearth (since [C] in the former is much lower, $\sim 0.02\%$, cf. Fig. 10.4). This high oxygen can be brought down to the open-hearth or the [C]-[O] equilibrium levels by deoxidising the Thomas steel with Thomas pig-iron or coke breeze.

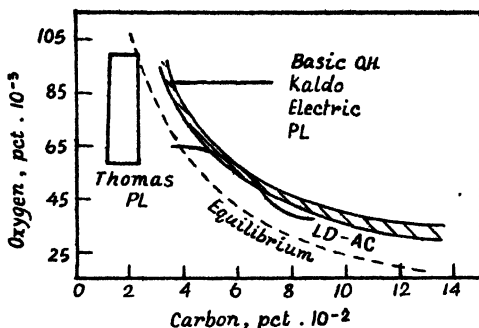


Fig. 10.4—Influence of carbon on oxygen in steel in various steelmaking processes.

Oxygen/air process¹⁶. There is no definite relationship between the oxygen and the carbon in the metal at the end of the process. However, the end-[O] is higher than in the normal Thomas process by about 0.01–0.02%. It is, however, lower than corresponding to the [C]-[O] equilibrium values (*cf.* p. 214).

Oxygen/CO₂ Process¹⁶: In this case also, the end-[O] is lower than the [C]-[O] equilibrium values but is higher than in the air or oxygen/air blown Thomas steel. But there seems to be a definite relation between [C] and [O] (*cf.* p. 214).

From Fig. 5.14, the air-blown steel contains the lowest and the O₂/CO₂-blown one, the highest end-[O]. Thus it appears that the large amount of aerial nitrogen in the normal Thomas process acts, in a way, as a deoxidising agent.

LD, LD-AC, PL Processes : There is a definite relationship between [C] and [O] in all these processes. The end-[O] is uniformly higher than the [C]-[O] equilibrium values and is of the same order as in the open-hearth. In the LD-AC, the equilibrium is approached (*cf.* Fig. 10.4)¹⁸ and in the PL,¹⁹ it is even crossed to lower values (*cf.* p. 295 and Fig. 10.4) below ~ 0.05% [C]. For LD^{14,17}, see Fig. 8.13.

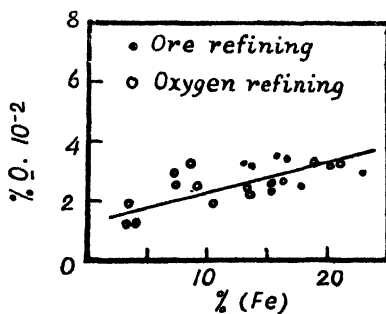
Kaldo; Rotor Processes : The metal oxygen follows the course as in the open-hearth and electric furnaces (*cf.* Fig. 10.4).

Electric steel : The final oxygen content of the liquid electric steel lies above the equilibrium [C]-[O] curve as in the case of open-hearth steel (see Fig. 10.4). However, in contrast to open-hearth, the [O] in the electric-arc furnace often approaches

and even reaches the equilibrium value at higher C-contents. The equilibrium value can only possibly be reached in the open-hearth and electric furnaces when the carbon boil, for some reason or other, ceases and comes to a standstill. In the open-hearth, the carbon reaction seldom ceases and continues to the end because of the oxidising atmosphere and, therefore, the [O] values are always higher than the equilibrium contents. However, in the electric furnaces a reducing atmosphere and thereby a stoppage of the boil can be effected at will; and hence, for any given [C] content, it is possible to attain the lowest, i.e. the most favourable equilibrium [O] values.

The above fact makes it possible to produce electric steel without necessarily invoking the reducing slag operation.⁵ The heat can be so managed as to bring the boil to a stop at the end before tapping and thus attain the equilibrium oxygen. This is seldom possible in the open-hearth.

The oxygen contents of the electric steel, at the end of oxidising refining by ore or gaseous oxygen lancing, vary from 0.025—0.040% according to the carbon-content.⁵ The reducing reaction which starts after running off the oxidising slag is achieved by additions like aluminium, when the oxygen is largely removed and a so-called *white slag* is obtained. Oxygen removal is rapid and in 10-15 minutes, oxygen as low as 0.01—0.02% is attained. Further reduction is only slow since the separation of solid alumina suspensions takes a long time (50-60 min).



[O] denotes oxygen in steel]

Fig. 10.5—Relation between oxygen in electric steel & iron in slag during refining with ore and oxygen, the carbon content being 0.12-0.20%. (K. G. Speith & H. v. Ende, Stahl und Eisen, 74, 1954, 520).

The [O]-content increases with (Fe)-slag at constant [C] as shown in Fig. 10.5. The influence of temperature cannot be detected as it is overshadowed by the greater effect of [C] and (Fe), although the oxygen solubility in steel increases with temperature. It can also be seen from the figure that the oxygen contents are similar whether the refining is performed with ore or with gaseous oxygen. Since the decarburisation rate in the latter case is much higher, it is evident that Schenck's concept (Eq. 5.8) is not applicable for the determination of oxygen during the refining of electric steel.

The lower the (Fe)-content of slag, the faster and nearer will be the approach of [O] to the [C]-[O] equilibrium. Therefore, after the initial high rate of decarburisation obtained by ore additions, the bath should be allowed to boil slowly without the further use of ore. The slag iron will be slowly reduced and the metal oxygen approach equilibrium with carbon.

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DEOXIDATION : NON-METALLIC INCLUSIONS

THE quality of steel depends not only on a proper control of metal and slag compositions, temperature, gases like hydrogen and nitrogen, etc. but also greatly on the oxygen content at tapping. A dirty steel results from an insufficient removal of oxygen by deoxidisers and/or inadequate separation of the products of deoxidation from the metal. The deoxidisers are elements having, as compared to iron, greater affinities for oxygen and whose products of oxidation are insoluble in and lighter than iron. It is only natural that the lower the end-oxygen the smaller will be the quantity of the deoxidation products and, therefore, the cleaner will be the steel. But, as already mentioned on p. 346, it is sometimes necessary to deliberately maintain a high oxygen during refining for the purpose of liquefying the high melting oxide particles in suspension in the metal, thereby facilitating their separation. This excess oxygen has to be removed by suitable means.

Diffusion deoxidation ¹

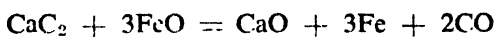
An obvious method for removing the end-oxygen to any desired extent is simply to create conditions in the bath and the slag so that [O] can migrate from the former to the latter. This is known as *diffusion deoxidation*. Oxygen transfer from metal to slag can only take place when the oxygen pressure or potential of the slag is less than that of the metal. In order to equalise the potentials in both the phases, oxygen from the interior of the metal must diffuse to the slag/metal interface where the slag can pick it up until an equilibrium between the two potentials is reached. Further transfer can take place if the equilibrium is disturbed by such reactions that decrease the a_{FeO} of the slag. Metal oxygen at any temperature is related to slag oxygen by $a_{\text{FeO}}, \%[\text{O}]_{\text{max.}} = \%[\text{O}]$. Since $[\text{O}]_{\text{max}}$ is constant at any temperature, [O] can only be lowered if a_{FeO} is reduced. The same is true with the concept of free oxide where $L = (\text{FeO})/[\text{O}]$ and,

therefore, the metal oxygen will migrate to slag as long as $[O] > (FeO)/L$. The lowering of a_{FeO} or 'free FeO' can be effected by (i) decreasing the basicity enormously, (ii) increasing the basicity in the range of basic slags, (iii) actively removing FeO from the slag with the help of reducing agents like ferro-silicon, carbon, aluminium etc. The possibilities (i) can be immediately discarded because of adverse effect on sulphur and phosphorus removal and (ii) is not feasible to any great extent since there is a limit to increase of lime. Only (iii) affords a practicable measure for reducing the slag (FeO). A decrease in temperature, though it reduces the amount of free FeO, has its own limitations.

In the open-hearth processes, the reduction of slag by means of carbon and silicon ($2FeO + Si = SiO_2 + Fe$; $FeO + C = CO + Fe$) is restricted by the oxidising furnace atmosphere which burns off large amounts of these substances. The atmosphere itself also supplies oxygen continuously to the slag. Yet a certain amount of deoxidation can be and is achieved by additions like ferro-manganese and ferro-silicon at the end of refining and a little before tapping. Such effects last for about half an hour, after which period the slag starts regaining its oxidising capacity. Even during this period, the diffusion is hampered by lack of turbulence since the carbon boil ceases for want of sufficient oxygen. In this respect, electric steelmaking in induction furnaces offers advantages because of the stirring action of the eddy current on the molten metal. A complete deoxidation, both in the open-hearth and electric furnaces, is hampered by the absorption of iron oxide (which has necessarily to be present during decarburisation) by the refractory lining. As the metal and slag are denuded of iron oxide, the equilibrium of the latter between the lining, metal and the slag is disturbed which results in the transfer of oxygen from the lining to the metal.

The advantages of diffusion deoxidation are greatly made use of in basic electric steelmaking, where the increase in or maintenance of the temperature does not need any oxidising heating gases and a reducing atmosphere can be achieved at will. Since, during decarburisation, the presence of an oxidising slag is a necessity, such a slag is replaced by a new one for subsequent bath deoxidation; otherwise, a rephosphorisation is bound to occur. This new slag, which is known as *reducing slag* and con-

sists mostly of lime, on its formation and liquefaction will itself withdraw a certain amount of oxygen from the bath so as to satisfy the physical law of partition between two phases. But this self-evident deoxidation does not proceed to an extent as to furnish such a clean steel as is expected and required. For more or less complete deoxidation, it is necessary to destroy the oxidising potential of the slag so that the metal oxygen can migrate to the slag unhindered. This is achieved normally by carbon in the form of coke, charcoal or graphite and also sometime by Fe-Al and Fe-Si. After the addition of the reducing agents, the slag progressively becomes whiter as ferrous oxide is removed and finally assumes a typical well-known 'grey' colour, caused by the formation of calcium carbide ($\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}$). This grey colour is an indication that the slag is completely denuded of FeO (i.e. deoxidation of the bath has been far-reaching, as a corollary) since, otherwise, the presence of an appreciable concentration of FeO would destroy the calcium carbide thus :



At such a stage, when deoxidation is more or less complete, the alloying of steel can be performed without any fear of formation of any oxides. The removal of oxygen takes, however, some time because of lack of turbulence, which can be artificially created by stirring with the hand or by the electric eddy currents as already mentioned.

We must be aware of the fact that the solubility of oxygen in steel decreases with temperature (cf. Fig. 3.2). Therefore, during casting, as the metal cools there is an automatic deoxidation. At the freezing point, there is an abrupt fall in the solubility and iron oxide separates out as a slag in the absence of any foreign element having a greater affinity for oxygen.

Precipitation deoxidation

In spite of the great advantages of the electric furnaces for obtaining low oxygen steels, in practice it has been found that the quality is below expectation and that a high residual oxygen is closely associated with cleaner and sounder castings. It is clear from Fig. 10.3 also, that a high oxygen is necessary, espe-

cially with low [Mn] heats, in order to liquefy the solid suspensions of oxides (from Si and Al in scrap) in the bath. Moreover, a vigorous boil is necessary for removing the gases, especially hydrogen, as well as to scavenge out the oxide suspensions. Such a boil can only be maintained with high metal oxygen. It has been the practice therefore, for basic electric furnaces, to use low carbon scrap from steel mills so that impurities like Si, Al, gases, etc. would be the minimum. Nowadays, it is not necessary for such furnaces to confine to such special variety of scrap whose availability is naturally small. This has been made possible because of our increasing knowledge of the methods for removing the oxygen completely from steel with proper use of deoxidisers which furnish liquid deoxidation products.

The purpose or the aim of the so called *precipitation deoxidation* is not only to remove oxygen by the formation of oxides that are insoluble in liquid steel but also to separate these lighter particles, which are formed within the metal and remain suspended in it, as far and as speedily as possible. These deoxidation products can climb to the surface of the metal rapidly if, according to Stokes' law, they are spherical in shape. Since, according to this law, the velocity of rising of any particle (under otherwise same conditions) entrapped in a liquid is proportional to the square of the radius of the particle, it is evident that the separation of the deoxidation products will be faster the greater their radii. Now, the spherical form can be attained completely only when the products are liquid. Moreover, these liquid droplets can undergo collision and coalesce and thereby grow larger and finally climb to the metal surface rapidly. It is no wonder, as long ago as 1928, Herty Jr and Fitterer² suggested that it should be the endeavour of steelmakers to obtain liquid deoxidation products. This has further won support from the investigation of Fischer and Wahlster.³ They have shown the presence of glassy silicates in soft steel which must have been liquid during or after their formation. Soon after Herty's suggestions, widespread investigations started for finding the conditions under which such liquid products could be obtained. Körber and Oelsen⁴ have been pioneers in this field.

Precipitation deoxidation can be carried out by any deoxidiser whose oxide is insoluble in the metal. These oxides being lighter

than the metal can rise to the metal surface, the velocity depending upon the densities of the oxide and of the metal, viscosity of the metal, size and shape of the oxides, spherical forms having larger velocity than any other shape. Assuming spherical shape, the velocity of rising of the oxides in liquid iron can be calculated by Stokes' law.

Example : According to Stokes' law, the rate of rise of the de-oxidation product is given by :

$$v = 0.222 \cdot g \cdot r^2 \cdot (d_m - d_s) / \eta \text{ cm. per sec.}$$

where

v = velocity of rising of the particle in cm. per sec.

g = gravitational constant = 981 cm. per sec per sec.

d_m = density of metal ; for steel with 0.1% C and 1,550°-1,600°C, the density is about 7 gm. per c.c.

d_s = density of inclusion or slag; it varies from 2.5 gm. per c.c.

η = viscosity of metal ; for liquid steel it is about 0.025 dyne-sec per cm.²

r = radius of inclusion particle.

From the above equation, for an Al-Mn-silicate with density of 3 gm. per c.c. and radius of 0.1 mm, $v = 3.3$ cm. per sec. and for radius of 1 mm. $v = 330$ cm. per sec.

The common deoxidisers used in steelmaking are : Mn, Si, Al and to a smaller extent Ti, V, B, Zr, Ca, etc. either singly or in combination. The densities of their oxides vary from 2 to 4 g/cm.³ The velocity of rising of the deoxidation products in liquid iron has been calculated by Ranque⁵ for different densities and particle size.

The affinity of the deoxidisers for oxygen have already been discussed under their individual equilibrium systems. A comparison is shown in common in Fig. 3.32. Amongst the usual elements used are Mn, Si and Al, the first having the weakest and the last the strongest deoxidising actions. The equilibrium systems of Mn, Si and Al, singly and together, in oxygen-containing liquid iron have already been discussed in Chap III.

Before considering these systems regarding the part they play in precipitation deoxidation, we would first familiarise ourselves with the various terms used in the process.⁶

Non-metallic inclusions: These are slag particles, i.e. the deoxidation products entrapped in steel during its solidification. *Indigenous* inclusions are those which develop from the oxidation products of elements used for deoxidation. *Exogenous* inclusions are those which originate from the refractories of ladles, launders, runners, stopper rods, etc. They can either be fluxed by the slag carried over to the ladle during tapping or by the deoxidation products themselves; or, they can directly enter the metal through mechanical erosion, fractures, etc.

Non-metallic inclusion may also originate from sulphur and nitrogen by forming multiple compounds.

Primary deoxidation products: The deoxidisers are generally added to the ladle during tapping. Since the chemical reaction between the oxygen in steel and the added elements is very fast, the deoxidation products are formed immediately. These may separate out or remain as suspensions in the liquid metal depending upon the density, viscosity of the metal and the oxides. The primary deoxidation products are those which are found in any sample of liquid metal. These may contain some of the suspensions carried over from the furnace itself due to their inability to separate out.

Secondary deoxidation products: Deoxidation cannot remove all the dissolved oxygen. At best, it can bring down the oxygen to the level in equilibrium with the concentration of the deoxidisers. Such equilibrium oxygen values are shown in Fig. 3.32 or can be calculated from the deoxidation constants of elements as discussed in the respective equilibrium systems, taking the temperature into consideration. But, during the solidification of steel in the ingot the conditions undergo profound change. As iron crystallises out, the rest metallic melt becomes progressively enriched with the dissolved elements including oxygen. The temperature also falls. These factors disturb the equilibrium previously attained and further reaction between the elements and oxygen occurs, resulting in the formation of fresh inclusions or *secondary deoxidation products*. Since these secondary products are seldom able to separate

out, it should be the endeavour to remove most of the oxygen as primary ones and attain the lowest possible equilibrium oxygen.

Total and dissolved oxygen : Oxygen in steel is usually estimated by the high temperature vacuum extraction process. The results include the oxygen contained in the suspended oxide particles as well as in the dissolved state. The amount of the suspended oxides should be very small if the refining of steel has been done satisfactorily, e.g. with a vigorous boil and slight over-oxidation, depending upon the [Mn]-content, for the liquefaction of silica and alumina suspensions. Dissolved oxygen becomes less and less as deoxidation proceeds and continues to do so during solidification. At the end, it becomes almost nil, because of its reaction with the increasing concentration of the deoxidisers in the liquid portions of the solidifying steel. The total oxygen decreases as the oxides separate out and, in the ideal case, should correspond with the equilibrium oxygen.

In order to obtain a clean killed steel with the least possible inclusions (solid or CO-blow holes), the following two conditions are to be fulfilled :⁶

- (1) The liquid steel in the teeming ladle should have the least possible equilibrium oxygen (i.e. dissolved oxygen) just before teeming in order to keep down the quantity of the secondary deoxidation products, which separate out with great difficulty, to the minimum.
- (2) The separation of the primary deoxidation products should be more or less complete before teeming starts.

The first requirement is not difficult if very strong deoxidisers are used, depending however, upon the desired specification of the finished steel. The primary problem of the precipitation deoxidation devolves upon the fulfilment of the second requirement.

In order to fulfil the second requirement, it was and still is assumed that liquid, coagulable, light deoxidation-products, large in size, must be aimed at to ensure their rapid and extensive separation from the liquid metal. Any deoxidiser, the melting point of whose oxide is above the temperature of liquid steel should, therefore, be unsuitable. Herty has in 1930 suggested the use of Mn-Si whose oxidation product, Fe-Mn-silicate, possesses lower melt-

ing point than that of iron through a large range of its chemical composition. We would now consider, in somewhat detail, the conditions under which the common deoxidisers Mn, Si, and Al may furnish, singly or together, the desired liquid oxides.

Deoxidation by manganese : The equilibrium reaction of [Mn] and [O] in steel has already been discussed in Chap. III. The oxidation product, MnO, forms a solution with FeO which may be solid or liquid depending upon [Mn] and [O] (or the ratio of FeO and MnO as per FeO-MnO phase diagram) at any given temperature.

It can be seen from Fig. 3.32 that Mn is not a very good deoxidiser. The oxygen content of steel, containing even small amounts of carbon, is much below the equilibrium value with regard to Mn and, therefore, Mn does not come into the picture of deoxidation of liquid steel. But conditions change during solidification in the ingot in the case of rimming steels (since in killed and semi-killed steels, the oxygen is lowered by stronger deoxidisers). Since carbon is a stronger reducing agent, the increasing concentrations of [C], [Mn] and [O] in the rest metallic melt would make [C] and [O] react preferentially, with the evolution of CO. But the evolution of CO depends on the p_{CO} as well as on the facilities of nucleation of bubbles. The ferrostatic head of an ingot plus the atmospheric pressure are equivalent to 1.7 atm. at a depth of 1 m and 2.7 atm. at 2 m. Therefore, at the bottom, the CO-evolution will be more suppressed than at the middle or at the top. At the bottom, with increasing concentrations of [Mn] and [O] and suppressed CO-evolution, there may be an inter-action between [Mn] and [O], provided decarburisation does not take place there. Whether the deoxidation product then formed under the special circumstances will be liquid or solid, depends upon the concentrations of [Mn] and [O] and the temperature in the molten portion.

Deoxidation by silicon : The equilibrium system of [Si] and [O] in liquid steel has already been discussed in Chap. III. The conditions, under which a liquid silicate may be formed, can be seen from Fig. 3.15. Even a small amount of [Si] in steel, e.g. 0.004%, with the corresponding [O]-content 0.06%, forms solid silica. Silicon is a much stronger deoxidiser than manganese.

It is known that the melting point of silica is lowered in the presence of MnO. Manganese silicate has a lower melting point than that of iron and, therefore, the simultaneous deoxidation with Mn-Si should produce liquid products, instead of solid silica, as in the case of pure Si. Surprisingly also, Mn and Si lower the oxygen in steel by a much greater extent than when each is used separately. This is clear from Fig. 3.32*b*.

Deoxidation with Mn and Si : The equilibrium reactions of [Mn] and [Si] with the oxygen in steel has already been discussed in Chap. III. From Fig. 3.32*b*, it can be seen that 0.05% Si and 0.5% Mn in iron are in equilibrium with almost half the amount of oxygen than is the case with 0.05% of pure silicon and in addition, the manganese silicate is still liquid at steelmaking temperatures.

The side view of Fig. 3.19 shows the relation between [Mn] and [O] when the steel contains varying amounts of silicon. The figure is valid for 1,600°C. At higher temperatures the curves shift upwards, i.e. the stability of oxygen in steel is increased; in other words, more [Mn] is necessary for reaching a definite oxygen than at lower temperatures. Thus, if the Fe-Mn-Si-O equilibrium has been attained at higher temperatures, the deoxidation proceeds automatically as the temperature falls, since the curves shift downwards. The side-view shows :

- (1) the oxygen content of steel in the presence of Mn is brought to low values by very small additions of silicon $\sim 0.05\%$, as compared to pure Mn-deoxidation shown by the FeO-MnO line.
- (2) the liquid deoxidation products, i.e. silicates can be obtained with high [Mn] even at low [O] and high [Si].
- (3) manganese takes part in deoxidation as long as liquid silicates are possible. The higher the [Si] the higher must also be the [Mn], so that the latter can take part in the reaction. In the region of solid silica, [O] is a function of [Si] only.

Fig. 11.1⁴ (a), (b) and (c) shows the action of silicon at 1,600°C on steel containing manganese with an initial oxygen content of [O]=0.105%. Deoxidation with Si alone furnishes solid silica along the line UX. One can add more Si, the higher the Mn-content of steel. At initial [Mn]=0.5% and [O]=0.105%,

the maximum Si that can be added is 0.17% without producing solid silica. During deoxidation, both [Si] and [Mn] are consumed.

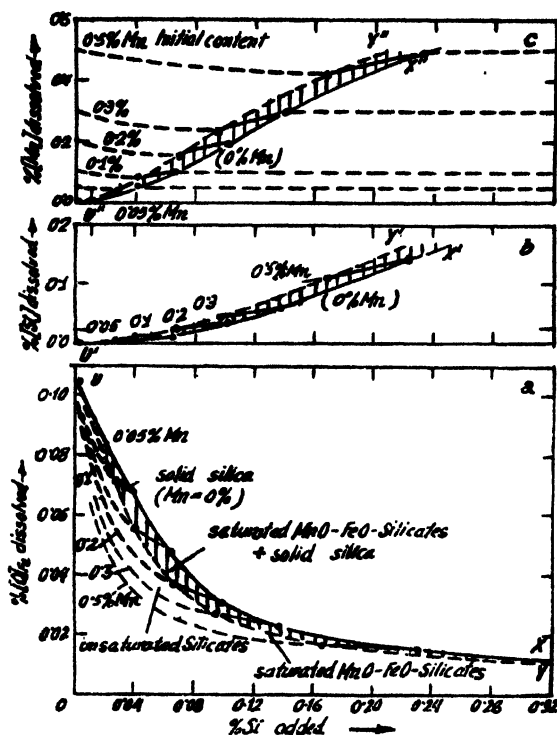


Fig. 11.1—Action of increasing silicon additions to liquid iron at different manganese contents at 1,600°C, the initial oxygen in steel being 0.105%. (Körber & Oelsen).

The elements remaining in the melt after deoxidation are respectively shown in Fig. 11.1 (b) and (c) and they are 0.11% Si and 0.42% Mn. If the amount of Si is more than 0.17%, the [Mn]-content increases (giving solid silica and liquid silicate shown in (c) by the shaded area), because the initial MnO formed is reduced by the excess silicon. An addition of Si in excess of that given by UX will always form solid silica. In such a case the manganese does not take part in the deoxidation reaction and its content remains unaltered as shown in Fig. 11.1(c).

It is clear from Fig. 3.18 that the formation or disappearance of

solid silica or liquid silicate is closely interlinked with the interdependent values of [Si], [Mn] and [O], and any two of the latter can fix the third. Herty Jr.² has suggested that one should aim at a Mn/Si ratio of 4:1 to 7:1 in liquid steel for obtaining a clean metal. He has been of the opinion that [Mn] must be several times higher than [Si] in order that enough MnO be present for the liquefaction of silica. Fig. 11.2⁷ shows the relationship of [Mn]

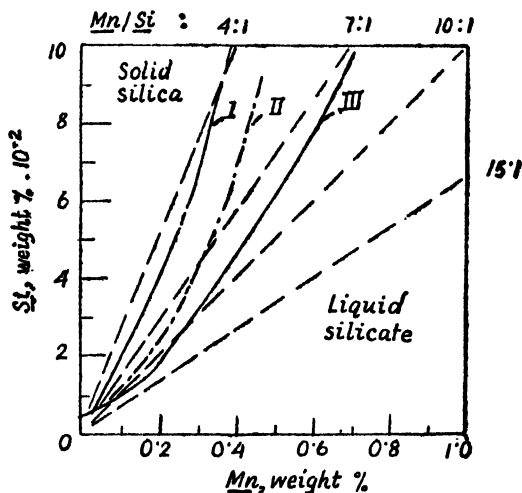


Fig. 11.2—Conditions for the formation of liquid deoxidation product while deoxidising steel with Mn & Si together. (H. Schenck, Stahl und Eisen, 77, 1957, 1446).

[The underlined elements denote their presence in Steel.]

and [Si] for the formation of liquid silicate. The ratios given above are drawn across the figure in dotted lines together with the higher ratios as well. Curve III is after Schenck and Wiesner⁸ at 1,540°C, whereas I and II are of Körber and Oelsen⁴ for 1,600°C and 1,500°C respectively. According to the latter work, the curves shift to the right with decreasing temperature. Although the curves of Körber and Oelsen fall within the range Mn/Si of 4 to 7, that of Schenck and Wiesner shows that even a ratio 7:1 is not sufficient for obtaining a liquid silicate below about 0.8% [Mn]. It may be noted that there is a slight inflection in the curves at low [Mn] contents. Below about 0.3% [Mn] the ratio should be above 10:1, or else, solid silica may develop.

From Fig. 11.2, a ratio of 7:1 is not always sufficient to produce liquid silicate. In practice as well, such a ratio does not always ensure the expected clean steel when Mn-Si alloy is added in the furnace or in the ladle. It is, therefore, advisable to use the least possible amount of silicon to bring down the initial high [O] and, later, add the required silicon for the purpose of alloying or complete killing. In many plants *spiegel iron* or open-hearth pig with low silicon is used for the same purpose, which furnishes liquid silicates and where the carbon in the additions acts also as a deoxidiser.

The effect of carbon, which is always present, should not be neglected, especially when the amount is large. It lowers the solidification range of steel and we have seen above that the boundary line of liquid silicates shifts to the right, i.e. to higher Mn/Si ratios, with decreasing temperature. Further, the increasing carbon concentration in the rest metallic melt of the solidifying ingot affects the activities of [Mn], [Si] and [O]. How such interactions would affect the possibilities of any liquid silicate formation cannot be predicted. To be on the safe side, it is usual to add small amounts of the strong deoxidiser Al, which removes extensively the initial high oxygen.

We have seen in Fig. 3.19 that, in the Mn-Si deoxidation, the higher the [Mn], the lower is the oxygen content that can be reached without entering the field of solid silica. This becomes clearer from Fig. 11.3. However, the lowest oxygen attainable with Mn-Si is of the order of 0.01% or a little lower, which is mostly unsatisfactory, and a stronger deoxidiser is necessary.

Deoxidation with Mn-Si-Al : Because of the very high fusion temperature ($\sim 2,030^{\circ}\text{C}$) of Al_2O_3 , one would expect solid deoxidation products from Al. Oelsen and Heynert⁹ worked on the possible liquid deoxidation products with combinations of Mn and Al. Curve III (Fig. 11.3⁷), based on their results, shows that for the same Mn, the oxygen required to liquefy alumina is much higher than that required to liquefy silica. And this is the case with a very low, almost unmeasurable, amount of Al. Therefore, for a significant amount of Al, the question of the formation of liquid aluminates does not arise.

The picture, however, changes if silicon is present in the system, which furnishes liquid Al-Mn-silicates. Such a liquid silicate as

well as a very low oxygen, lower than in the case Mn-Si alone (Curve I Fig. 11.3), can be attained by the use of Mn-Si-Al as shown by Curve II (see also Fig. 3.32*b*).

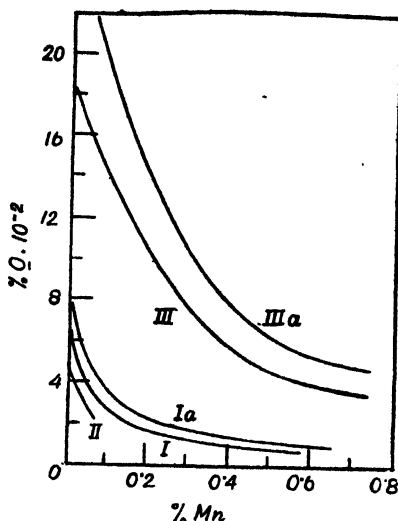


Fig. 11.3—Conditions for liquefaction of silica & alumina suspensions in liquid iron at 1,540–1,550°C. Curve I, for liquid Fe-Mn-silicate; II as I, with 20% alumina; III for liquid aluminat. Ia & IIIa as I & III but with metal containing 0.5% C. (H. Schenck, Stahl und Eisen, 77, 1957, 1147). [O denotes its presence in steel.]

To summarise⁷, it is possible to attain a low oxygen in steel by deoxidising with Mn-Si and simultaneously obtain a liquid deoxidation product, which is so very important for the cleanness of steel. But, one must be careful to maintain the Mn/Si ratio very high; thereby, an [O]-content of the order of 0.01% can be attained without difficulty. However, in combination with a small amount of Al \sim 0.03%, i.e. 0.3 kg/t of steel, the oxygen can be lowered to about 0.001% without any danger of formation of solid products. It is, of course, sometimes necessary to achieve still lower oxygen contents, or more of Al may be necessary (1 kg/t) for fixing the nitrogen. Under such circumstances, the oxygen should be brought down to a low value with low-Al Mn-Si combination and the final rest of aluminium, when added, will find only a small amount of oxygen and the fine solid alumina suspensions then formed will not be harmful.

Koch and Wever¹⁰ have shown (Fig. 11.4) the effect of relative proportions of Mn, Si, Al for obtaining a low content of inclusions. High Si/Al ratios yield much cleaner metal.

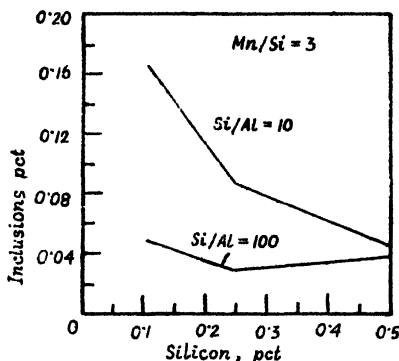


Fig. 11.4—Relationship between inclusions and silicon contents with different ratios of Si & Al. (W. Koch & F. Wever, *Stahl und Eisen*, 74, 1954, 264-71.)

Recent experiments on deoxidation confirm what has been said in the foregoing discussions but indications are there which do not conform to these ideas. Plöcklinger and co-workers^{9,11} have shown that using Al alone, in contrast to these ideas, the primary high alumina inclusions separate out several times faster than the silicates formed from Si. According to Plöcklinger and Wahlster⁹, Si forms liquid coagulable silicates instead of solid silica. The importance of turbulence on the velocity of separation of oxide inclusions has come to light. Born and Wittstruck¹² have shown that only a very small amount of inclusions is retained from a rimming metal. Also, in their experiments on deoxidation of Thomas steel with Al, Plöcklinger and Rosegger¹¹ have found that tiny alumina particles separate out even in the ingot because of turbulent currents in the liquid steel.

In order to verify these new findings, Plöcklinger and Wahlster⁹ have carried out numerous deoxidation experiments with liquid steel containing 0.08-0.10% oxygen and using Si, Ti, Al, Zr, MnSi, CaSi, CaAl and other deoxidisers.

Deoxidation with silicon furnishes, immediately after the addition, liquid, well-coagulable, homogeneous silicate inclusions with 98% SiO₂.

With Ti, in a short time, large oxide inclusions of 90% TiO_2 are formed which are not uniform and look like sintered mass. Deoxidation with Zr gives ZrO_2 with m.p. $2,700^\circ\text{C}$ and the inclusions are small and contain 93% ZrO_2 . In some regions, coagulation does occur and, therefore, larger particles could be isolated with size up to $10\ \mu$ or so.

Deoxidation with Al gives rise to, within 30 sec., primary products with $\sim 97\%$ Al_2O_3 . Most of these contain nuclei of the liquefied oxide with fine oxide particles sintered around them.

In the case of silico-manganese, the size and shape of the primary products containing 20-30% MnO are similar to those formed from the silicon deoxidation reaction. The coagulation in this case, however, continues for several minutes after the addition. The same happens with silico-calcium as well.

In short⁶, the addition of deoxidisers alone or as ferro-alloys to liquid steel containing oxygen produces, initially, liquid oxides which may coagulate or sinter together according to their nature and the prevailing conditions. The reaction is very rapid and only products with low melting points can continue to coagulate for a longer period. The question arises why even the high melting oxides (except perhaps ZrO_2) do form, at least initially, liquid oxides and grow in size in a very short time. The fluxing action of FeO is not answerable for the phenomenon since only up to 10% of this oxide has been found in the inclusions. No plausible reasons are afforded but amongst other possibilities, it may be that locally very high temperatures are attained when the deoxidisers react with oxygen in steel, giving out enormous heats of formation of their oxides.

The behaviour of different deoxidisers is shown clearly in Fig. 11.5⁶. One can see three distinct categories :

- (1) Some deoxidisers like Si, SiMn, SiCa, when added to steel in the ladle during tapping, show relatively small amounts of oxygen removal in the first couple of minutes but the oxygen decreases continuously for some time after the tapping is complete.
- (2) Deoxidisers like Al, Ti, FeAl, CaAl, remove most of the oxygen, which attains low values immediately after the addition and their solution in steel. The oxides formed

separate out rapidly. A prolonged stay in the ladle does not lead to any further diminution of oxygen.

- (3) Although Zr has a great affinity for oxygen and lowers [O] to a great extent and, initially, a part of the oxide formed separates out rapidly, yet the steel contains a considerable amount of total oxygen or inclusions. This is due to the unfavourable physical properties of the oxide particles and, even after a prolonged stay in the ladle, the particles do not separate out.

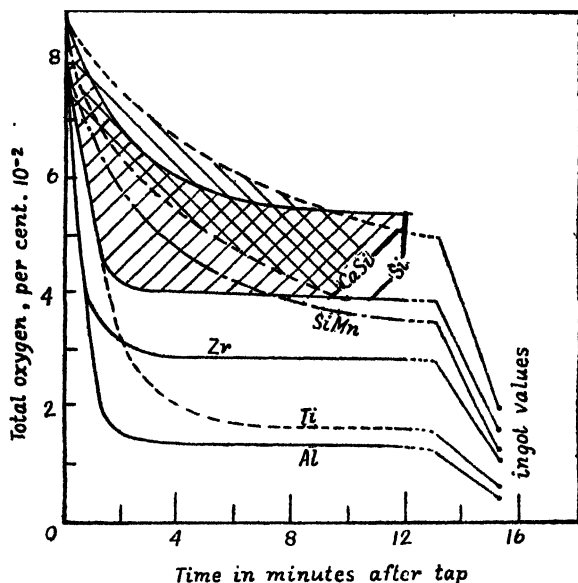


Fig. 11.3—Variations in the total oxygen in steel after addition of various deoxidisers. (E. Plocklinger & M. Wahlster, *Stahl und Eisen*, 80, 1960, 666).

During teeming there is a further separation of the oxides in the ingot which continues up to the moment of complete solidification.

A striking phenomenon, however, is that neither the size nor the density of the primary oxidation products determines the speed and extent of their separation from liquid steel. It has been found that in the first 3 min. after tapping, during which period a turbulence in the ladle metal is discernible, small particles of oxides of Zr separate out as rapidly as the much larger Ti-oxide

inclusions. Also, inclusions of the same size, e.g. alumina and silicate, show a different behaviour in their separation. Aluminium brings [O] rapidly down to 15% of the initial value, whereas silicon with a slower speed of separation brings it to only 50%. It is clear that the separation of the inclusions is not dependent on the particle size in a turbulent bath. The effect of the density is equally surprising. Silicates with a density of 2.3 should separate out more rapidly than the heavier oxides of Al and Ti (density of oxides 3.9 and 3.8 respectively); in fact, however, they do not do so.

It is surmised that the surface properties have a role to play in the separation of the deoxidation products. Al_2O_3 and ZrO_2 are scarcely *wetted* by liquid steel with low oxygen contents: whereas, silica-rich silicates and glasses show a good 'wettability' because of free valencies on their phase interfaces. The influence is strengthened by the higher oxygen content in silicon-deoxidised steel, which imparts a smaller surface tension on the liquid steel as well as a smaller interfacial tension on the oxide inclusions than in the case with very low oxygen steel, when Al, Zr and Ti are used as deoxidisers.

During the stay of the ladle after the end of tapping, i.e. from 3 to 12 min., the turbulence in the metal ceases. However, a thermal movement is still present, which is not enough to separate out particles less than the critical size ($\sim 10 \mu$). Oxides of Al and Zr, smaller in size, remain in the metal. Since their m.p. are higher than that of steel, they no longer coagulate and grow bigger.

Deoxidation products of Si and, especially of SiMn, because of their lower m.p., can and do grow larger through coagulation. In spite of their unfavourable wettability properties, they rise up during the stay of the ladle because of the size factor only.

The physical conditions during teeming are similar to those occurring during tapping in the ladle. A turbulence (mechanical) is caused which enables the particles to separate out but, somewhat, slowly, since the higher viscosity of the metal at lower temperatures resists such movements upwards. One must also take account of the secondary deoxidation products formed, during solidification, from the oxygen left over after the deoxidation reaction.

A very clean fully-killed open-hearth or electric steel generally contains about 0.004% total oxygen, the amount of inclusions not exceeding $\sim 0.01\%$ by weight; whereas, an average basic open-hearth steel may contain 0.008% of total oxygen and 0.01-0.025% of inclusions. It is not difficult to obtain steels with cleanness of this order in the open-hearth because they are tapped at much higher temperatures (50° - 60°C higher) than the Thomas ones. The greater cleanness of the former variety as compared to the latter can be attributed to the following factors, (i) low viscosity of steel at higher temperatures, (ii) the possibility of allowing more time at high temperatures for the separation of the deoxidation products, and (iii) low initial oxygen contents of the open-hearth steels, especially at high C-contents, as compared to Thomas varieties. Open-hearth quality Thomas steel with low-[P] and low-[S] is generally tapped at lower temperatures; this lower temperature and the presence of the deoxidation products in suspension, both increase the viscosity of the steel which, in order to minimise the radiation losses, has to be teemed soon after tapping. An addition of 0.12-0.25% Si to the steel, alone or with 0.4 Kg Al/t, gives inclusions ranging from 0.05 to 0.130%, which is extremely unsatisfactory. Such steels, if killed by 0.29% Si with 0.1-0.2% Al, contain much less of inclusions, as found in the open-hearth varieties; whereas, if killed with 0.2-0.5% Al alone, they can be compared with the cleanest open-hearth or electric ones.

It is believed that aluminium is, by far, the best deoxidiser. Castings made from aluminium-deoxidised steel are generally sound and free from pinhole porosity.^{13,14} Even calcium, which, according to the free energy data, is a more potent deoxidiser than aluminium, when used as a complex with Si and/or Mn does not lower the oxygen content of steel sufficiently¹⁵ as to prevent the pinhole porosity.

There is a distinct advantage in deoxidising by carbon since the product is a gas and escapes. Low carbon steel having a high residual oxygen can be deoxidised to a certain extent by recarburising and oxygen values, corresponding to C-O equilibrium, may be reached. Degasification under vacuum serves the same purpose, but to a much greater extent (*cf.* Chapter XIII).

NON-METALLIC INCLUSIONS ¹⁶⁻¹⁸**Indigenous inclusions**

We have defined non-metallic inclusions on p. 361. These are mainly oxides and sulphides but nitrides and carbides are also included in the family. The causes of the formation of indigenous inclusions are :

- (a) reactions of oxygen, sulphur, nitrogen with deoxidisers and denitrifiers.
- (b) oxidation reactions occurring during refining, tapping or teeming.
- (c) separation of soluble constituents during cooling and freezing.
- (d) progressive change in the equilibrium constants with falling temperature and the change in the concentrations of various elements in the rest metallic melt during solidification, resulting in the precipitation of the insoluble products.

A greater part of the insoluble inclusions originally formed separates out while the metal is still liquid. But due to factors (c) and (d) above, they continue to be precipitated from the metal during cooling and freezing. They are, therefore, always in equilibrium with the metal as far as permitted by the reaction rates and diffusion of the reactants. Their compositions thus become dependent on the composition and temperature of the metal. Their size and shape depend upon whether they precipitate as solid or liquid. The solids are constrained to remain as small particles and are crystalline (except the glassy precipitates which do not crystallise). The liquids remain as globules and are larger in size due to coagulation. Some inclusions, especially sulphides, are very soluble in steel and precipitate from the last portions of the rest metallic melt and deposit on the primary grain boundaries.

Oxides : The mechanism of formation of oxide inclusions can be understood from the equilibrium systems of Mn, Si, Al and others described in Chapter III. Their oxides may appear singly or together, depending upon their relative amounts as well as on the temperature and oxygen content of steel.

In the rimming steel, only FeO-MnO inclusions are formed which may be solid or liquid depending upon the conditions (*cf.* Fig. 3.9). Since manganese is always present in steel, a silicon deoxidised steel may contain solid silica or liquid iron-manganese-silicate. Their compositions have been discussed in Chapter III. In the presence of small quantities of aluminium, it is possible to get liquid aluminates. Larger additions of Al produce solid alumina with other oxides. Alumina is sometimes found incorporated in the silicate or sulphide inclusions. Some inclusions have already been described in the section on deoxidation in this chapter.

Inclusions of silica and alumina formed from the respective elements accompanying pig-iron and scrap can be solid or liquid depending upon the manganese and oxygen contents of steel (*cf.* Fig. 11.3).

Sulphides : The sulphides constitute more than half the amount of inclusions in steel. Manganese is the most important of all sulphur binders because of its presence in much larger amounts compared to other elements. Other sulphides, e.g. Al_2S_3 , ZrS , TiS , CrS , CaS , etc. are possible but their concentrations are relatively small. Their solubilities in steel are much less than that of MnS except in the case of TiS . (An excess of titanium induces a eutectic sulphide formation). These are all soluble in MnS and, therefore, seldom occur singly. The important sulphide systems and the role of manganese in forming sulphide inclusions have already been discussed on pp. 134-37.

Oxygen is invariably present in steel and it lowers the solubility of FeS - MnS therein. Such inclusions are precipitated earlier and they tend to form globules.¹⁹ Non-killed and silicon deoxidised steels (where a little oxygen is always left) show such type of inclusions. In the case of a steel, completely killed with just enough quantities and no excess of deoxidisers like Al, Zr, the solubility of FeS - MnS increases and they precipitate as eutectics on the grain boundaries with the last metal to freeze. Such a metal shows low ductility values. But when an excess of these deoxidisers are present they form sulphides, which being less soluble, precipitate earlier and grow larger. The ill-effects of sulphur are much reduced in such cases.

Nitrides : We have discussed on p. 132 the relative affinities

of a few elements for nitrogen. Amongst these, aluminium assumes a great importance since it is invariably added to steel during tapping and teeming for deoxidation and fine-grained structure. It reacts with nitrogen to form a nitride, AlN , which precipitates when the equilibrium product is exceeded. According to Darken *et al.*,²⁰

$$\log (\% [\text{Al}] \cdot \% [\text{N}]) = -7.400/T + 1.95$$

The precipitation is slow at high and low temperatures but is rather rapid in the intermediate range²¹, around 800°C. The precipitation of nitrides partly removes the ill-effects of nitrogen. Other nitrides are also possible, e.g. nitrides of Zr, B, Ti. They have practically no solid solubility in steel and precipitate as cubic crystals during the freezing of the metal.

Carbides¹⁷: Stable carbides of titanium and columbium are possible when they are present in sufficient quantities. These carbides are insoluble in solid steel and precipitate when the metal reaches the freezing temperature.

Exogenous inclusions

The chief sources of these inclusions are; (a) products of metal-refractory interaction, (b) entrapment of slag, (c) mechanical erosion of refractories (d) slag-refractory corrosion and entrapment of the products. These are discussed briefly below:

- (a)^{22,23} Manganese in steel can react with the silica of the alumino-silicate refractories in the ladle, launder, stopper rods, runners; the MnO thus formed fluxes the refractory. The fluxed material becomes incorporated in the metal and is entrapped in the ingot during solidification. These reactions are probably aided by high metal temperature which softens the refractories. Such inclusions have been found to closely resemble the composition of the casting pit refractories and consist mainly of MnO , SiO_2 and Al_2O_3 . The attack by the manganese in steel will be less, the higher the refractoriness, i.e. the higher the alumina content of the material and the lower the $[\text{Mn}]/[\text{Si}]$ ratio.

According to Morton and Carter,²⁴ the ferric oxide, Fe_2O_3 , present in the refractory is attacked initially by manganese and iron and the resulting liquid FeO-MnO slag fluxes the refractory.

A slag, $\text{FeO-MnO-SiO}_2\text{-Al}_2\text{O}_3$, is taken up by the metal, the amounts of FeO and MnO depending upon the Mn- and Si- contents of the metal. Thus, a low- Fe_2O_3 refractory should be more resistant to metal attack, which has been shown experimentally by these investigators.

- (b) The slag formed during steelmaking may be physically entrapped in the metal. In the acid process, the composition would naturally be FeO-MnO-SiO_2 with some CaO and Al_2O_3 . In the basic process, the inclusions will consist of CaO, MgO, MnO, SiO_2 , P_2O_5 , CaS, FeO, Fe_2O_3 , mostly as compounds.
- (c) Liquid steel is always in contact with refractories, from the furnace onwards, till it is poured in the moulds. Since these refractories are mostly alumino-silicates, their fusion temperatures are only a little higher than the temperature of the liquid steel. This slight advantage is also wiped out by the fluxing action of FeO and MnO. Thus the refractory surface in contact with the metal is more or less in a fused state or at least soft enough to be eroded away by the metal stream. Most of these, however, float out but some may be trapped in the freezing ingot. They are generally of large size and can be easily recognised from their structure. In order to reduce their occurrence, only high grade refractory materials should be used and patching work done with basic refractory materials.²⁵ Steel should also be poured hot since its high fluidity would allow the entrained inclusions to float to the surface easily (Stokes' law).
- (d) Slags are extremely corrosive at high temperatures. The action of basic slags on alumino-silicates is much more than that of acid slags. Lime and, to a smaller extent magnesia, attack the fire-clay bricks and form multiple compounds with silica and alumina which dissolve in the slag but some may be entrained in the metal.

The subject of non-metallic inclusions is a vast one. The causes of their occurrence have been discussed, which is the purpose of this section. For a detailed study, the reader may refer to other sources.^{18,25,20}

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CHAPTER XII

GASES IN STEEL

THE presence of gases in steel deteriorates its quality. Investigations have led to the identification of mainly CO, H₂, N₂, together with small amounts of CO₂, H₂O, O₂ and CH₄. The latter four may, however, be neglected. The evolution of the former three during solidification of the metal may give rise to *wild, bleeding ingots*; the gases may also be entrapped and give rise to *blow holes*, which cause flaws in the finished products unless closed by welding during hot working. The evolution of the gases not only adversely affects the mechanical properties of steel but causes segregation as well.

The solubility of hydrogen and nitrogen in steel follows Sievert's law (Eq. 1.20) and their evolution pressures increase as the metal cools down. The evolution pressure of CO also increases, since the concentrations of carbon and oxygen increase in the rest metallic melt during solidification. The gases can evolve inside the ingots if their total evolution pressure exceeds the sum of the pressures of the atmosphere and the ferrostatic head. The tensile strength of steel, measured in atmospheres, must be added to the latter pressures if the formation of a gas bubble in the solid metal involves fracture of the material.

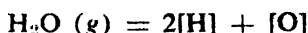
HYDROGEN

General

The presence of more hydrogen than corresponding to its solubility at the melting point of steel causes unsound and porous ingots and castings. Hydrogen, in amounts 0.0006—0.0012%, can cause such defects in steel depending upon the amount and nature of the alloying elements. Ingots made from steel with lower hydrogen contents are not immune from defects. They cause abnormal reduction in the ductility and reduction of area values. A marked sensitivity to flaking occurs when hydrogen exceeds about 0.0002%. The hair-line crack is generated by

the high evolution pressure of hydrogen at low temperatures (due to low solubility and consequent precipitation of the gas), which exceeds the tensile strength of steel. Both these phenomena affect hot rolling and forging; they may also initiate fatigue cracks in service components. It is true that considerable amounts of hydrogen can be removed by proper heat treatment. This is possible because of the high diffusion velocity of the gas in steel, which increases with temperature. But, for thick cross-sections, it becomes uneconomical since a prolonged heating is necessary. By doubling the cross-section, the time necessary is about four times for the same degree of hydrogen removal. Steels with enlarged γ -field take longer because the diffusion in this variety is much slower than in the α - or δ -ones.

Electric and Open-hearth Furnaces:^{1,2} The chief sources of hydrogen in steel are the furnace atmosphere (water vapour, unburned hydrocarbon or hydrogen), slag, moist slag-formers or other additions, moist or oily scrap as well as the refractories (launder, ladle, runners, etc.). The moisture reacts with steel according to :



The equilibrium oxygen and hydrogen contents of liquid iron in the presence of humid atmosphere at various partial pressures of water vapour are shown in Fig. 3.35. It is paradoxical that, at low oxygen contents, the metal can take up more hydrogen from a moist atmosphere than from a pure hydrogen atmosphere. This is probably because, while a thin film of slag or oxide is permeable to water vapour, it does not permit the escape of hydrogen. Thus, it rather absorbs atomic hydrogen than give up molecular hydrogen.³

From Fig. 3.35, steel absorbs $\sim 0.0006\%$ from a pure hydrogen atmosphere of $p_{\text{H}_2} = 0.05$ atm. But, a well-killed steel or steel from under a reducing slag in the electric furnace can take more hydrogen from an atmosphere with $p_{\text{H}_2\text{O}}$ of only about 0.003 atm. It is not surprising, therefore, that considerable quantities of hydrogen can be absorbed by steel in the open-hearth and electric furnaces. In the open-hearth the products of combustion contain about 25% by volume of water vapour besides the

moisture contents of the additions. On a hot summer day, with relative humidity of 80-90%, the electric furnace atmosphere may contain 4-6% of moisture; whereas, in cold winter with humidity 40-45%, the moisture content may range from only 0.35-0.40%. Again, the relative humidity may vary by even 100% during a course of a few hours. Thus, for making a good quality steel, the melters have to be careful all the time. Various workers⁴⁻⁶ have found a correlation between the relative humidity and the frequency of occurrence of 'bleeding' ingots.

During steelmaking in the furnaces, hydrogen can be taken up from the furnace atmosphere either in the melt-down period, when bare scrap is exposed directly to the combustion gases, or through the slag layer which acts as a barrier. The other source is, of course, the moisture in the charge. From Fig. 3.35, it is clear that the hydrogen absorption will be lower, the higher the state of oxidation of the bath. This lends support to the observation in practice that heats, worked and tapped hot, yield products with much better physical properties and less rejects. This is probably because such heats invariably mean high residual oxygen in the bath. In electric steelmaking, especially during the wet summer months, the melt down period is of importance. The smaller the melting time and the higher the oxygen the bath carries, the lower will be the hydrogen to start with. But, in the open-hearth processes, the summer and winter months should have no influence on the melt-down hydrogen since the furnace atmosphere itself contains a considerable amount of moisture.

It has been demonstrated by various workers⁸⁻¹¹ that the acid open-hearth steels contain much less hydrogen than the basic ones (difference, usually $\sim 0.0002\%$). This may be the reason for the fact that acid steels are less susceptible to hair-line cracks than the basic ones. Some of the values are given in Table 12.1 together with those of other processes. This difference in the acid and basic open-hearth steels can only be due to the part the slag plays in these two processes, since, the furnace atmospheres in both the cases are identical. It is not exactly known in which form does the hydrogen exist in slags. It may be as hydrogen or HO^{12} or H_2O^8 . The total hydrogen contents of the acid and basic open-hearth slags as well as those of the basic arc oxidising ones are given in Table 12.2¹. The average hydrogen content

of the basic open-hearth slags is 0.0063% and that of the acid ones is about a third of this value. This may account, partly at least, for the higher hydrogen contents in basic steels. It can be seen from the tables 12.1 and 12.2 that the hydrogen contents of slags are much more than that of steel.

TABLE—12.1
HYDROGEN AND NITROGEN IN STEEL

<i>Steelmaking Process</i>	<i>Hydrogen %.</i> 10 ⁻⁴	<i>Nitrogen %.</i> 10 ⁻⁴
Acid open-hearth	3.8	80-80
Basic open-hearth	5.6	"
Basic electric arc	4.4	"
Acid Bessemer		100-200
Basic Bessemer (normal Thomas)	4.5 (liq. steel)	"
" " (oxygen-enriched)	4.5 " "	40-80
" " (oxygen-steam)	5.14 " "	20-40

TABLE—12.2
HYDROGEN IN SLAG

<i>Steelmaking Process</i>	<i>Hydrogen %.</i> 10 ⁻⁴
Acid open-hearth slag	10-35
Basic " "	50-75
Basic electric arc " (oxidising period)	40-70

Equilibrium experiments with the slag and a moist atmosphere show that the hydrogen content increases with the partial pressure of water vapour. At 1,550°C a slag, under pure vapour, may contain hydrogen 0.09-0.11%; whereas, under the air, the same slag at the same temperature contains 0.0001-0.002% hydrogen.¹ In the electric arc furnace, the dry atmosphere and the double slagging result in a lower hydrogen in the slag than in the case of basic open-hearth.

Hydrogen delivered to steel by the furnace atmosphere, whether directly or through the slag layer, can escape only when its evolution pressure is high and exceeds the sum of the atmospheric and ferrostatic pressures (meaning that the liquid steel must be super-saturated with hydrogen, which does not happen) or when the bubbles of other gases are present whose hydrogen partial pressure is less than that in the metal. Such sources are the bubbles of CO or CO₂ evolved during the carbon (or lime) boil, into which

hydrogen diffuses from the steel at the gas(bubble)/metal interface and leaves the metal with the ascending gas stream. Therefore, the hydrogen in the metal would depend upon the difference between the amount escaping and the amount delivered by the slag. Since the amount escaping increases as the gas/metal interfacial area increases, it is apparent that a vigorous carbon boil would have greater *scavenging* or *washing* action on hydrogen^{13,14}. This is clear from Fig. 12.1^{14,12} which shows the theoretical hydrogen content of steel as a function of time for different rates of carbon boil. The course the hydrogen follows and its relation to carbon removal have been computed by many from acid, basic and electric hearth heats. The results indicate that the lowest hydrogen is reached during the boil, i.e. in the decarburisation period^{8, 14-16}.

There exists, during the boil, an apparent equilibrium between the hydrogen absorption by the metal and the washing action of CO. Provided there is a vigorous boil, the initial hydrogen concentration should not affect the end-content of the gas. High moisture bearing additions, under such circumstances, do not necessarily lead to a high hydrogen in the finished steel. The vigour, not the duration of the boil, profoundly affects the metal hydrogen.⁴ Here again we realise the importance of Schenck's suggestion¹⁷ of refining with slags at a basicity ratio of about 2.7, where the activity of (FeO) is the maximum (*cf.* Fig. 4.5). The resulting high bath oxygen does not only help the manganese to flux the solid suspended particles of silica and alumina present in the bath (*cf.* Fig. 11.3), but it also increases the decarburisation rate (with the resulting washing away of hydrogen); and further, according to Eq. 3.53, a high oxygen can only be in equilibrium with a low hydrogen and thus the excess gas will be obliged to escape as and when facilities, such as bubbles, occur. For low hydrogen steels, the rates of decarburisation prescribed are: basic open-hearth $\sim 0.5\% \text{C/ hour}$; acid open-hearth $0.2-0.3\% \text{C/hour}$.^{4,8}

The additions made to the furnace during steelmaking should be very dry, especially if they are in large lumps since they pass through the slag layer and come directly in contact with the metal. Light materials lose their moisture to the furnace atmosphere during the interval they remain in the slag.

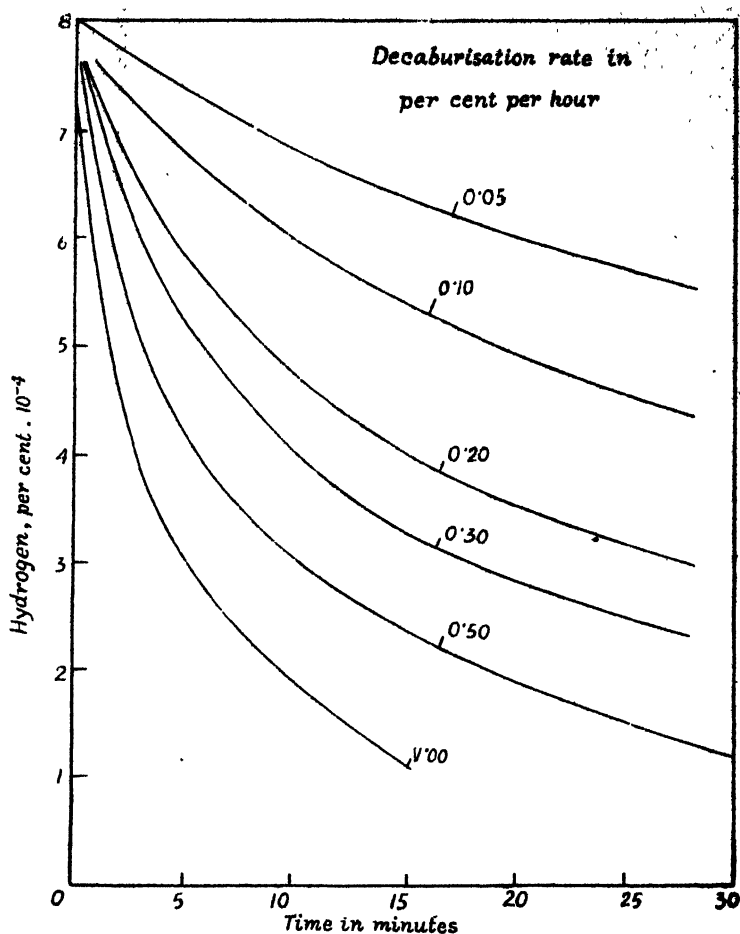


Fig. 12.1—Theoretical washing action of evolved gases on hydrogen in steel at different decarburisation rates.

The deoxidisers used also contain considerable amounts of hydrogen.^{9,15} These may cause an increase of the gas in the metal, more so when the bath is blocked, since the washing action of the boil becomes absent and also a low oxygen in the metal would enable a higher amount of hydrogen to remain in equilibrium. During this period, the hydrogen content shows an increase in both the acid and basic open-hearths, caused by the reaction of the slag and the metal with the furnace gases. It is,

therefore, advisable to tap the metal as soon as possible after the bath has been blocked. The blocking in the ladle should be more advantageous. In the electric furnace, the ingredients added for making the 'reducing slag' should be dry in order to prevent a late hydrogen pick-up.

Hydrogen pick-up of over 0.0002% has been reported by Barraclough¹⁸ and Sims *et al*⁴ from moist refractories during tapping and teeming. A freshly lined ladle may cause an increase of 0.0001%, whereas the same ladle, after a couple of heats, shows an increase of only 0.00003% hydrogen. A considerable amount of the gas may also be absorbed from the ingot moulds themselves.¹⁴ A profusely tar-coated mould shows much higher hydrogen (by even 0.0004%) in steel than in the case of a clean uncoated mould.¹⁹

Barraclough¹⁸ has compiled the approximate hydrogen contents of basic electric-arc fully killed steels of different varieties for sound, unsound and wild ingots (*cf.* Table 12.3).

TABLE-12.3

Type of steel	Hydrogen per cent $\times 10^{-4}$ in ingots *		
	Sound	Unsound	Wild
Unalloyed	6.0	6.0- 7.5	7.5
Low alloy	6.5	6.5- 8.0	8.0
Stainless Chrom	9.0	9.0-11.0	11.0
Stainless Chrom-nickel	11.0	11.0-12.5	12.5

* 0.0001% H = 1.11 cm³. H/100 gm.

In conclusion, the following should be carefully observed for producing a low hydrogen steel¹ :

- (a) a vigorous boil be maintained for 'scavenging' the hydrogen
- (b) all additions made, especially after the boil, must be very dry. Lime is the most potent source of moisture in the electric furnace.
- (c) the launder, runners, ladle and the ingot moulds must be dry in order to ward off the hydrogen absorption during tapping and teeming.
- (d) in the acid and basic open-hearths, the metal should be tapped as soon as possible after the 'block'.

It has been found that with all the efforts, it is difficult to produce steel with hydrogen lower than 0.0004%. For still lower hydrogen, the vacuum stream-degassing (*cf.* Chap. XIII) is probably the only answer. By this method it can be brought down to about 0.0002% or less. One has to consider, however, the cost of vacuum treatment which ranges from £2.3 per ton.²⁰ But, on the other hand, a large piece for forging would take 2-3 weeks for annealing and driving out the gas by diffusion. One other way is to bubble inert gases like argon, helium (nitrogen also can be used but its content in steel increases, rendering the latter unsuitable for special varieties), through the liquid metal or direct a high pressure jet of the gases on it through the slag cover. It is, however, difficult to bring the hydrogen down below 0.0003%.

Pneumatic Processes : The amounts of hydrogen in steel, produced in the converters,²¹ are shown in Table 12.1. They are generally less than in the hearth furnaces. This is because of the scavenging action of the aerial nitrogen and the very high rate of decarburisation, of the order 15-25% C/hour, which is about 30-50 times higher than in the hearth furnaces. A special mention will be made here of the oxy-steam process^{21, 22} since, contrary to normal expectations, the hydrogen content of steel in this case is only slightly higher than in the conventional practice, although an enormous volume of steam is used ($O_2 : H_2O$ from 1 : 1.0 to 1 : 1.5). At the end of the blow, the partial pressure of water vapour is 0.2-0.3 atm. and, therefore, the theoretical [H]-contents (for $[O]=0.05-0.09\%$) should be 0.002-0.004%; but, the actual figures are 0.0004-0.0010% as can be seen in Fig. 3.35, shaded areas *a* and *b* respectively. (The equilibrium [H]-[O] diagram is from Carney *et al.*^{8 11}). The average value is about 0.0004% when the steam is stopped during the final blow, after the first slag-off, in the case of 'fine' dephosphorisation. The conditions during the final blow are highly oxidising and the air or oxygen-enriched air used in this period have a certain scavenging action. Both reduce the hydrogen content greatly. In contrast, the second-slag period in the electric furnace is highly reducing and there the danger of hydrogen absorption is considerable.

The hydrogen contents of the ingots and finished products are much less than that of liquid steel because of the deoxidising and

rimming actions as well as the diffusion of hydrogen during storage. These are shown by the areas *c* and *d*.

NITROGEN

General

The solubility of nitrogen in steel and its deleterious effects on the physical properties of the metal have been discussed in Chapter III. High nitrogen steels are unsuitable for deep drawing purposes. On the other hand, the element imparts certain properties which are useful for some varieties,²³ viz. Cr-Mn and Ni-less stainless steels. Like oxygen, it is possible to fix the nitrogen by denitrifiers such as Al, Ti, B, Zr, etc. Hydrogen cannot be removed or fixed by any such elements. Hitherto, the open-hearth steel had been considered ideal for its low nitrogen contents, 0.003-0.008%. For the air-blown converter steel, the range is 0.010-0.020%. In the open-hearth, the nitrogenous atmosphere is separated by the slag layer; whereas, in the converter processes the aerial nitrogen is in direct contact with the metal. The danger is more when the dead weight of nitrogen passes undiluted (by CO gas) at the end of the blow, because the solubility increases as the partial pressure of nitrogen rises. It is remarkable that a high nitrogen ($\sim 0.016\%$) has been observed in melts from the electric induction furnace.²⁴ This may be probably because the aerial nitrogen has free access when the slag cover is pushed aside by the turbulent motion of the eddy currents or because the coke, used for making the reducing slag, itself supplies nitrogen.

Some nitrogen values are given in Table 12.1. The nitrogen content of open-hearth steels is low because of the washing action of the decarburisation reaction and almost a complete lack of any direct contact of nitrogenous atmosphere with the metal. Great efforts have been made in the last decade to produce low-phosphorus and low-nitrogen steels in converters, comparable to open-hearth varieties. The phosphorus problems have been discussed in Chapter VIII. We will devote, in the following pages, mainly to the nitrogen absorption in various pneumatic processes.

It may be noted here that the nitrogen absorption increases with (a) temperature (b) partial pressure of nitrogen (c) time and

intimacy of contact. Since these factors are common in all the pneumatic processes, we will discuss each briefly :

- (a) The temperature should not be allowed to rise excessively. The minimum temperature is, however, limited by the teeming requirements and pouring techniques. An excessive rise can be controlled by the addition of steam to the blast or ore, millscale, scrap, to the bath. The reactions of steam and iron oxides with the bath are highly endothermic and, therefore, both are superior to scrap. A comparison of various coolants is given in Table 12.4.

TABLE-12.4

EFFECT OF VARIOUS COOLANTS COMPARED TO SCRAP

1 m ³ steam	7 Kg scrap
1 m ³ carbon dioxide	9 Kg scrap
1 Kg Ore (60% Fe)	2 Kg scrap
1 Kg lime-stone	2.1 Kg scrap

- (b) An addition of steam or carbon dioxide to the blast reduces the partial pressure of nitrogen. We should be aware that when the dead weight of nitrogen ascends undiluted through the metal in the converter, in the absence of the carbon reaction and when the oxygen forms only non-gaseous oxides, the p_{N_2} is about 1.3 atm. (sum of the atmospheric and ferrostatic pressures). The partial pressure is reduced if the converter is blown oblique or through the sides or the bath depth is low. An old converter lining with a new bottom gives much lower nitrogen because the depth is lower for the same weight of metallic charge. Contrary to usual belief, the oxygen-enrichment does not reduce p_{N_2} in the Thomas after-blow period.²⁸ Even with 95% oxygen, the $p_{N_2} = 0.95-1.00$ atm. In the case of oxy-steam blow, $p_{N_2} = 0.05-0.10$ atm. during the after-blow.
- (c) The removal of metalloids depends upon the amount of oxygen supplied. The real variable is the oxygen input and not the time. Therefore, additions of oxidising agents like oxygen, steam, carbon dioxide, ore, millscale, etc.

shorten the time of blow and reduce the volume of nitrogen, thereby reducing the nitrogen absorption. Low bath depth also reduces the time of contact of nitrogen. The same effect is obtained in the oblique or side blowing. The latter two reduce the intimacy of contact considerably.

It may be mentioned here that the pig-iron from the blast furnace contains very low nitrogen, 0.003–0.006%, although the partial pressure of nitrogen in the furnace is about 1 atm. Steel contains larger amounts because of subsequent pick-up during refining. The low values are probably because of the low temperature of iron and the reduced solubility of nitrogen in the presence of carbon and silicon (*cf.* Fig. 3.38). These become apparent from the following equation of Darken and Gurry:²⁶

$$\log \% [N] = -0.86 - 0.06\% [\text{Si}] - 0.24\% [\text{C}] + 0.015\% [\text{Mn}] - 1000/T$$

Acid Bessemer : In the acid Bessemer, the final nitrogen is of the order of 0.015–0.020%. If it is assumed that nitrogen at approximately 1 atm. is in direct contact with the metal, the content should be much higher, viz. 0.04%. It seems the equilibrium is never reached. From Fig. 2.2, the calculated nitrogen solubility (dotted line) follows the observed values closely in the initial stage but the latter fall off rapidly later. According to Darken and Gurry,²⁶ this is because, at the early stage, nitrogen is in direct contact with the metal, the products of oxidation being either permeable solid silica or gaseous CO. After a period, a thin liquid oxide film forms a barrier and retards the absorption of nitrogen. It follows that a low nitrogen should be associated with cold blows or any other blow where the silicon is oxidised early.

The final nitrogen can be reduced to $\sim 0.002\%$ if the metal is blow with oxygen/steam mixtures (60:40 ratio). If the bath depth is reduced to a third, nitrogen $\sim 0.01\%$ can be realised.

Basic Processes

Thomas or basic Bessemer : The final nitrogen content of the Thomas steel is similar to its acid counterpart. Dardell²⁷ sug-

gests the following equation for the effect of carbon and phosphorus on the solubility maxima of nitrogen in liquid iron.

$$\log \% [N] = -1.61/T - 0.721 + \frac{1}{2} \log p_{N_2} - 0.0092 (\% Fe_3P + \% Fe_3C) \text{ where } p_{N_2} \text{ is in atm.}$$

According to the equation, the absorption of nitrogen during the Thomas blow is slow at the beginning when carbon and phosphorus are present in considerable amounts. The absorption increases at the end when most of them have been removed, i.e. during the after blow period (cf. Fig. 2.3).

The mechanism of nitrogen absorption has been discussed on p. 131. As long as the system remains oxidising and the temperature remains low, the absorption is sluggish. It begins to rise when the temperature is high and the oxygen potential has decreased suddenly after the transition due to extensive dephosphorisation (cf. Fig. 8.3). According to Kosmider and Schenck,²⁸ the absorption is facilitated under reducing conditions and retarded under oxidising conditions. This knowledge and the experience of many workers have led to various modifications of the blowing technique, viz. oblique and side blowing, oxygen enrichment of air, oxy-steam and oxy-carbon dioxide mixtures, additions of oxidising agents before the transition when nitrogen is low, etc. for obtaining low nitrogen steels. It may be noted here that due to profuse decarburisation, the initial nitrogen, 0.006—0.008%, decreases to a minimum of 0.003—0.004% in about 30—50% of the blowing time.

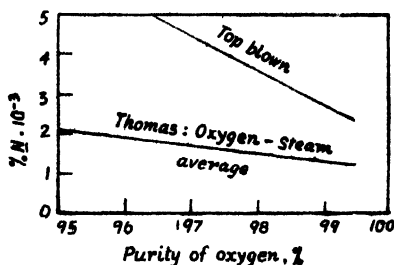
HPN and LNP: These processes make use of ore or millscale before the transition, while the nitrogen is still low. The progress of the blows is shown in Fig. 2.4. Such additions keep the bath oxidising during the critical period of nitrogen absorption, i.e. just before and after the transition. They promote early formation of oxidising slags, decrease the duration of the blow as well as the finishing temperature. Nitrogen content is below 0.01% in the liquid steel.

Oxygen-enriched air: Oxygen-enrichment of air serves almost the same purpose as the ore or scale in the HPN or LNP processes. The enriched blast can be used throughout the blow but is usually done when the blow has gone halfway. Nitrogen content is below 0.01%.

Oxycarbon dioxide²⁰: The introduction of carbon dioxide to the blast is done when the blow has gone about halfway with air. This reduces the consumption of the expensive gas. The time of blow is shortened to 12 min. as against 16 min. with air. The cooling effect of CO_2 is much more than that of H_2O , as is clear from Table 12.4. The nitrogen content is below 0.01%.

Oxy-steam²²: This is by far the most rapid process. The time of blow is only about 8 min. The progress of the blow is shown in Fig. 2.5. At certain stages during the blow, the decarburisation rate can be as high as 1% C/min and the dephosphorisation rate 0.8% P/min. The lime is liquefied early since about 50% of the phosphorus is removed before the transition. If only an oxygen-steam mixture is blown throughout, the nitrogen content ranges between 0.002—0.003%.

In fact, however, the nitrogen range in Haspe, Germany, is 0.003—0.005%. This is because a two-slag process is usually employed for producing very low-phosphorus steel, $\sim 0.02\%$, comparable to the open-hearth quality. When the phosphorus has reached 0.06—0.12%, the first slag is drained off as much as possible and the metal reblown for 20—45 seconds with air or oxygen-enriched air, with or without additions of slag formers like lime dust and soda. Some nitrogen is, naturally, introduced during reblowing but the steam is deliberately avoided in this period in order to wash away some of the hydrogen.



[N denotes its presence in steel.]

Fig. 12.2—Influence of purity of oxygen on nitrogen content of steel in oxygen-steam and top-blown processes. (H. Neuhaus, H. Kosmider & P. E. Hardt, *Stahl und Eisen*, 81, 1961, 1381-88).

The amount of nitrogen introduced in the steel depends upon the purity of oxygen (*cf.* Fig. 12.2²²). The average values at

Haspe are higher than those in Belgium or in the Steel Company of Wales. The reason is apparent from the above discussions.

Oxygen Processes : The dependence of nitrogen absorption on the purity of oxygen in the top-blown oxygen process is shown in Fig. 12.2. With oxygen purity of 96—97%, the nitrogen can be as high as in the open-hearth steel (0.004—0.006%). This nitrogen content is obviously higher than that in the modified basic Bessemer processes using oxygen, although, in this case, dephosphorisation precedes decarburisation, the washing action of the carbon boil continues to the end and there is no after-blow, during which period the tendency for nitrogen absorption is the greatest. The reason for such a behaviour may probably be attributed to the much longer duration of the blow and the high local temperature where the oxygen jet meets the metal.

It is possible to obtain steels with 0.004—0.006% nitrogen using even 85% pure oxygen, if water is injected into the oxygen lance to act as a coolant. It is a very effective means for suppressing the high local temperature of the reaction zone and thus controlling the nitrogen content of the metal. The use of water may not, however, be economical as the cooling effect decreases the amount of scrap that can be melted in the LD or other oxygen steelmaking processes.

CARBON MONOXIDE

Unkilled steel forms the major portion of the world production of commercial steels. This is not only because the unkilled steel is cheaper and discards are less, but also because of its good surface and thick skin, free from segregations, which help in its shaping.

The evolution of CO during casting of ingots is of utmost importance in the production of unkilled steel. As we are already aware, the equilibrium products of carbon and oxygen in liquid iron are 0.0025 at 1,600°C and 0.0020 at 1,500°C. However, the actual values of the tapped steels in the ladle range between 0.0045—0.0060, depending upon the carbon content. Due to the lack of facilities for nucleation, there is seldom any rim or effervescence in the ladle, although the products exceed the equili-

brrium values. The condition changes on pouring the metal in the mould when the temperature drops and the metal starts freezing, the iron crystals separating out serving as nuclei. The first portion to solidify consists of more or less pure crystals of iron and, as the freezing proceeds, the residual liquid becomes progressively enriched in carbon, oxygen and others of which manganese only is of importance in unkilld steels. The carbon-oxygen reaction is a function of pressure; it proceeds freely on the surface but it is more and more inhibited, as the depth increases in the mould, due to the ferrostatic pressure of the ingot head. This means that the reaction between C and O starts at a lower temperature the greater the ingot head, i.e. the distance from the metal level. In other words, the CO evolution will occur when the cooling has progressed far, the metal viscosity has increased and the dendrites have extended farther into the liquid which result in the retention of any gas evolved, between the dendrites, as blow-holes. It is, therefore, understandable that an increased presence of surface blow-holes is observed in the lower third of the rimming steel ingots.

We have recognised in our discussions on pp. 77-80 the important role the manganese plays in controlling the volume of the CO gas, evolved during solidification of the rimming steel. Whether Mn or C will react with oxygen and to what extent, depend upon the ingot head and the enrichment of the residual melt in Mn, C and O. For low-Mn, the evolution of CO may proceed unhindered throughout the ingot after the metal skin has formed, because C and O will react before the equilibrium concentrations of Mn and O are reached in the residual melt. In such a case, the metal will rim wildly and rise in the mould. For medium-Mn steel, the CO will evolve at first throughout the solidifying metal; the intensity will slowly subside as the volume of the residual melt narrows down and the manganese is in a position to react to form FeO-MnO deoxidation products. These are, generally, confined in the middle zone of the ingot. For each variety of good rimming steel with thick and clean skin, there is an optimum medium-Mn concentration range (about 0.3% Mn) depending upon the carbon content, mould temperature, teeming rate and teeming temperature.

If the Mn-concentration is too high, the deoxidation products

will form earlier, rendering the melt thick and dense, which impedes the passage of the small amounts of gas formed. Some of the gas may be entrapped, leading to blow-holes near the ingot surface.

It is recognised that the manganese plays a vital part in adjusting the volume and the moment of CO evolution so that a balanced ingot with thick skin can be obtained. We have also seen that when its concentration lies on the left of AQ or AM of Fig. 3.9, there is a possibility of the formation of a liquid FeO-MnO slag which can rise easily to the surface. It has, however, been found that considerable quantities of inclusions remain inside the ingot, especially in the lower third portion. They do not cause much trouble during rolling when present in uniformly distributed and finely divided form. When present as small lumps, they lead to sticking of sheets and trouble in the modern fast deep-drawing processes. According to Kosmider *et al*⁸¹, an ingot with sufficient cleanness can be obtained if, for a definite C-content, the oxygen content is in the higher and the Mn-content in the lower ranges. They suggest that in the case of capped bottle-top mould, where the CO-reaction is inhibited by increased pressure at the ingot top, the oxygen should be rather low and manganese high. This is because the inferior washing action, caused by slow evolution of CO, does not help the inclusions to come to the top. The high manganese suppresses the C-O reaction and forms solid MnO (plus FeO) which remains throughout the ingot in a finely divided form.

The modern fast deep-drawing processes need steel with greater cleanness. It has been found that aerial oxidation during teeming and solidification of the metal contributes the major amount of the inclusions. The initial inclusions formed come up on the ingot surface but they disappear when they begin to solidify or thicken at the end of teeming. It is surmised that due to a convection caused by the evolution of CO, these inclusions are sucked down inside the metal. The convection current flows upwards along the ingot wall and moves down from the centre at the top.⁸² The appearance of the inclusions in the lower third of the ingot is probably due to their entrapment during the circulation because of increased viscosity of the metal at the bottom. The suction is greater the more profuse the CO evolution. According

to the calculations of Kosmider *et al*⁸¹, the maximum evolution of CO, for any given $[C].[O]$ product, occurs when the C-content lies between 0.06—0.08%. Above and below this optimum range, the amount of CO evolved in litres per ton of metal decreases. Therefore, between 0.06—0.08% $[C]$, the suction downwards in an ingot will be the maximum.

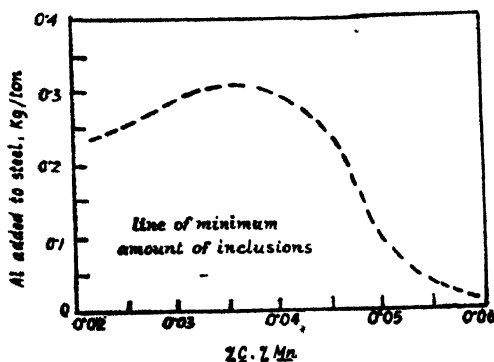


Fig. 12.3—Line of minimum amount of inclusions in mechanically capped rimming steel with Al additions depending upon the product C and Mn. [The underlined elements denote their presence in Steel.]

In order to obtain very clean rimming steel, therefore, the aerial oxidation should be avoided, the CO evolution suppressed and the deoxidation products formed be liquid, so that wherever inclusions are formed they might rise to the surface (i.e. the Mn-content should be on the left of line AM, Fig. 3.9). Baare *et al*⁸² suggest that the mould should be covered by a thick steel plate after a short interval on the completion of teeming and the metal should be deoxidised by aluminium to an extent that the CO evolution may not lead to any suction towards the bottom. They calculated the amount of aluminium to be added for obtaining minimum amount of inclusion for any given $[C].[Mn]$ product in the metal. This is shown in Fig. 12.3.

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CHAPTER XIII

VACUUM DEGASSING OF STEEL

THE manufacture and pouring of steel in vacuum are gaining wider and wider applications. Vacuum-treated steel shows higher plasticity and continuous strength and increased resistance to corrosion. The improvement in the mechanical and other properties is due to the lower contents of gases and non-metallic inclusions. The substances possible to remove are the elements whose solubility in steel or whose reaction products are dependent on pressure. The gases of major interest that must be removed are oxygen and hydrogen and to some extent nitrogen. Oxygen does not escape in an elemental form but as CO, a product of the reaction with carbon in the metal. In the case of hydrogen and nitrogen, their percentages in the melt are functions of the partial pressures of the gases over the melt, i.e. they follow Sievert's law. The carbon-oxygen reaction is directly proportional to the partial pressure of carbon monoxide in the gas phase (*cf.* p. 65). Both the elements can be brought to low values under reduced pressures, when the reaction $[C] + [O] \rightarrow CO(g)$ proceeds to the right markedly. The equilibrium relation at 1,600°C is:

$$\% [C] \cdot \% [O] = 0.0025 \cdot p_{CO} \quad 13.1$$

Removal of Oxygen

The theoretical oxygen in steel, attainable under vacuum, depends both upon the then [C]-content and the p_{CO} . The above equation is reasonably valid at high pressures as well as at pressures in the range 760 to 1 Torr. According to Beck¹ and Knüppel *et al.*,² an [O]-content less than about 0.002% cannot be achieved. At 100 Torr, the [C]-equivalent to this amount of oxygen is about 0.2% and at 10 Torr, about 0.02%. Under these pressures, an addition of carbon to the melt will not reduce [O] below 0.002%, i.e. the melt will no longer be in equilibrium with [C] and [O]. This is because, at very low oxygen values, the metal is replenished by the element from the ladle lining or

from the oxide inclusions already present. Further, in cases where vacuum treatment is effected without any agitation or turbulence, i.e. in the absence of any nuclei for CO-formation, the carbon reaction is suppressed due to ferrostatic and surface tension forces; the oxygen, in such cases, is always found to be above the equilibrium value. An approach to equilibrium is only possible, as in 'stream degassing', where liquid steel is automatically atomised due to forces of evacuation; or, where nuclei are provided by the introduction of an inactive foreign gas, like argon.

Apart from the reaction of the metal with the lining, there is a further possibility of the metal reacting with the slag. The reaction of liquid metal with liquid slags is much faster than that with solid slags or refractory materials. If an already vacuum treated liquid steel comes into contact with any liquid oxide slag, the metal picks up oxygen until the equilibrium is reached. It is, therefore, essential that the slag be removed to the greatest possible extent before the metal is subjected to evacuation. The portion of slag remaining behind may be rendered ineffective by the addition of burnt lime or dolomite.

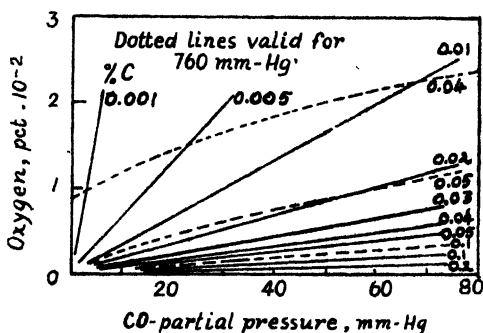


Fig. 13.1—Carbon & oxygen contents of liquid steel at very low partial pressures of CO. (F. Harders, H. Knüppel & K. Brotzmann, *Stahl und Eisen*, 76, 1956, 1722.)

During the carbon reaction, it is not only the oxygen that is removed but it is accompanied with an equivalent amount of carbon. The solid lines in Fig. 13.1³ show the theoretical equilibrium [C] and [O] values at various p_{CO} . However, during the C-O reaction, both the elements decrease simultaneously and the dotted lines show how both change from definite initial values

at 760 Torr, when subjected to vacuum. This figure is an enlargement of the low pressure region. As for example, an iron melt with initial contents of 0.05% [C] and 0.05% [O], when subjected to vacuum, should give values of 0.02% [C] and 0.009% [O] at 50 Torr (follow the dotted line 760 Torr-0.05 C. This line meets the solid line for 0.05 C at 760 Torr in the high pressure figure, not given here.) If the same line is followed, at 5 Torr the respective concentrations would be 0.014 % [C] and 0.002 % [O]. Such low pressures are obtainable to-day without difficulty in large-scale vacuum treatment plants.

The deoxidising action of carbon is enormous at low pressures. Below about 0.05 atm, it exceeds the deoxidising action of the strongest deoxidisers (*cf.* Fig. 3.32). There is a further advantage that the product of deoxidation is a gas which escapes from the system. Therefore, the primary as well as the secondary indigenous oxide inclusions formed during precipitation deoxidation, which are never completely removed ordinarily, can be avoided if the liquid steel is made, treated or cast in *vacuo*. Theoretically, there should be no objection to additions of moderate amounts of deoxidisers or alloying elements. Such additions bring the [O] down to the respective equilibrium values. A portion or the whole of the added element is oxidised and forms inclusions, or goes over to slag. If the equilibrium [O] becomes less than that corresponding to [C]-equilibrium at 1 atm, then carbon and oxygen will not react until the external pressure is brought down low-enough, so that their concentrations exceed the values given by the low-pressure equilibrium curves (*cf.* Fig. 3.32). In such a case, the low-oxygen melt will not be in equilibrium with the oxide inclusions and these will be reduced to their elements. However, this reducing reaction is very slow compared to the C-O reaction, which determines the overall rate of the vacuum degasification process.

As with the inclusions, the refractories are also capable of reacting with the melt but their reaction velocity is smaller than that with the slag or the inclusions. The reaction may be minimised by reducing the time of contact between the molten steel and the refractory materials. The time, however, depends upon the rapidity and the extent of CO-evolution.

The velocity of degasification is important not only because of

the above but also a longer interval causes a considerable fall in the temperature (which also depends upon the volume of gas evolution), with the consequent teeming difficulties. Hardly 20-25 minutes remain at the disposal for treating 75-100 tons of steel. The velocity of carbon reaction depends upon the surface factor, apart from the total pressure and the value of the $[C].[O]$ product. In the vacuum-lift process, the surface area for degasification is about $8 \text{ m}^2/\text{t}$ of steel.² This enables a strong boil to take place. The process is accelerated so much (due to the enlargement of surface area) that a greater part of oxygen is removed from steel placed under vacuum for ~ 0.4 min. It is, however, necessary to make steel at higher temperatures than usual (about $30^\circ\text{--}40^\circ\text{C}$ higher), when it is intended for vacuum treatment.

It is possible,⁴⁻⁸ through the vacuum treatment of steel with $[C]$ up to $\sim 0.5\%$, to bring the oxygen content from $0.02\text{--}0.03\%$ to such a low value as 0.002% . Usually, the range is $0.004\text{--}0.010\%$. The total amount of the inclusions formed by precipitation deoxidation is considerably less in vacuum treated than in non-treated steel. Alumina and silicates are greatly reduced and whatever is left in the bath remains uniformly dispersed in a finely divided form throughout the cast metal. The amount of the inclusions differs according to the different methods used in casting. Tix *et al*⁸ have indicated about 0.003% inclusion in steel cast into ingots under vacuum⁹. If the oxygen after treatment is on the low side, it may not be necessary to use any deoxidiser at all for making killed steel. Vacuum-treated open-hearth steel has been used for alloying with silicon without any significant formation of inclusions. Aluminium, about 0.2 Kg/t , has been used for fixing nitrogen as well as for obtaining fine grains in the ladle-degassed steel, without its cleanness⁴ being affected.

There is, however, the possibility of an oxygen absorption during pouring of the degasified steel. It is advisable, therefore, to protect the metal from aerial oxidation by the use of inert gases or the exclusion of air as under vacuum.

Removal of gases

The gases of importance dissolved in steel are hydrogen and nitrogen. They are dissolved in an atomic rather than in the

molecular form. They obey Sievert's law and, therefore, their solubilities are proportional to the square root of their partial pressures. As a consequence, their dependence on the pressure is much less than in the case of the $[C]-[O]$ reaction where the $[C]$ and $[O]$ contents are directly proportional to the partial pressure of CO . The sources of these gases in steel, their solubilities and relation to partial pressure have been described in Chapters III and XII.

The decrease in the external pressure effects a drop in the solubilities of the gases. But it is only the surface layer of the metal which is affected. We know that for gases to evolve, nuclei have to be present. Otherwise, either the pressure build-up has to be high for the gases to escape or the amount of the dissolved gases should exceed the equilibrium contents under their prevailing partial pressures. In the case of ladle degassing, it is possible for gases in the surface layer, exposed to the evacuated atmosphere, to escape; whereas, in the deeper layers, where a high ferro-static pressure prevails, it is difficult for them to do so. Therefore, their evolution becomes a function of their rates of diffusion from the interior to the exposed surface. Hydrogen can escape more easily because of its higher diffusion rate in steel. The removal of the gases is, however, facilitated during the vacuum treatment because the bubbles of CO evolved themselves provide the nuclei. A foreign inert gas should, therefore, accelerate the process since it not only presents fresh nuclei but facilitates CO evolution as well. This washing action (by argon) has been used in the vacuum-lift process.

Hydrogen can normally be reduced by about 40-50%. The higher the initial content, the greater its removal. Normally about 2-3 $cm^3/100$ gm. of steel can be attained.^{4-5,9,11} This is shown in Fig. 13.2⁴ where values obtained from a few processes are given. It can also be seen that the hydrogen content follows Sievert's law closely.

It is doubtful whether nitrogen can be removed to any extent. A reduction by about 40% has been reported but, in this case, the initial nitrogen content was high (Bessemer steel, 0.018-0.030% N).¹¹ Tix *et al*⁵ have found similar reduction in steel, not greatly deoxidised with the help of Al and Ti. Nitrogen con-

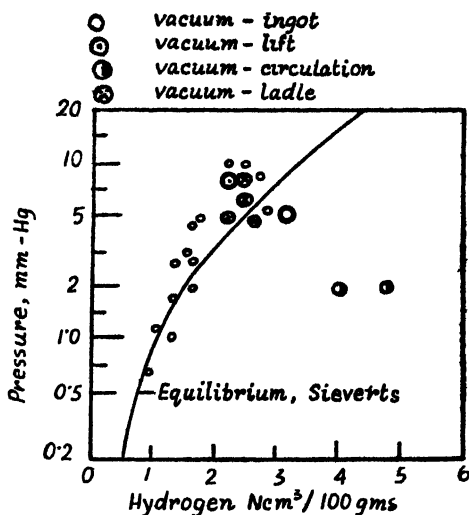


Fig. 13.2—Hydrogen contents of steel at very low pressures in various vacuum degassing processes. (K. G. Speith, H. v. Ende & A. Pfeiffer, *Stahl Und Eisen*, 80, 1960, 741).

tent also depends upon the presence of alloying elements. (Cr, Al, V, cause an increase while C, P, decrease it.)

Degassing Methods ¹⁰

Ladle degassing : The ladle containing liquid steel is placed in a larger air-tight vessel suitable for evacuation (*cf.* Fig. 13.3a). The large and efficient pumps now-a-days available can evacuate such large vessels and reach a pressure of 5-10 Torr in 10 min. Even 1 Torr can be achieved. Apart from the slopping of metal and slag over the edge of the ladle caused by their rise due to suction, another disadvantage of ladle degassing is the inhibition of gas evolution for lack of nucleation. This can be circumvented by introducing gases like argon, helium, at the bottom through a refractory tube from above or by causing a stirring action by induction.

Stream degassing :¹² In order to obtain a more effective degassing by enlarging the metal surface, the liquid steel from a tundish is allowed to stream into an air-tight vessel connected to vacuum pump and containing the teeming ladle. The suction tears apart

the stream at an angle of almost 90° , i.e. the droplets take almost a horizontal direction for some distance before falling in the teeming ladle. The diameter of the stream at a depth of 1.5 m may be 3-4 m which is about 8-10 times that of the stream poured in air (Fig. 13.3d). The time taken for a 40-50 ton cast is hardly 10 min. and the temperature loss 30° - 40°C .

Vacuum-lift process :³ This process is based on sucking the liquid steel from the pouring ladle through a suction column to a height of ~ 1.4 m, into a heated vessel connected to exhaust pump. After about 12 tons of the metal have gone in, the vessel with the column is raised by crane so that the metal level reaches the neck of the column, as shown in Fig. 13.3b. The metal inside the heated vessel flows back to the ladle. This is repeated, e.g. in an 80 ton ladle it is cycled for about 30 times which means that the entire steel flows for about 5 times through the degassing vessel. The treatment takes ~ 20 min. and the pressure reached 2-10 Torr. The heating arrangement is necessary because of large temperature loss, $\sim 85^\circ\text{C}$.

Circulation process :¹⁸ This process is similar in principle to the vacuum-lift process. There are two suction columns emanating from the vacuum vessel which is placed on the pouring ladle by crane. These columns immerse in the liquid steel. One of them, called the rising column, is provided with a hole on the side through which argon gas is fed in quantity, ~ 100 litres/min. As the vessel is evacuated and the steel rises in this column, the argon expands due to heat and low pressure. Thus, it not only 'washes' the gases in steel but also has an atomising action and the metal splits into droplets in the vacuum vessel (Fig. 13.3c). The droplets fall due to gravity and pass through the second column to the metal reserve in the ladle. A continuous circulation is thus set up whose rate is about 13 t/min. The loss of temperature is $\sim 30^\circ\text{C}$, which can be minimised by induction heating arrangements.

Ingot casting :¹⁴ The principle is the same as in stream degassing except that the ingot mould is directly placed in vacuum and the casting is made out of contact with air. This method seems to be the most advantageous and about 60-70% reduction in the gases is possible. A device is illustrated in Fig. 13.3e.

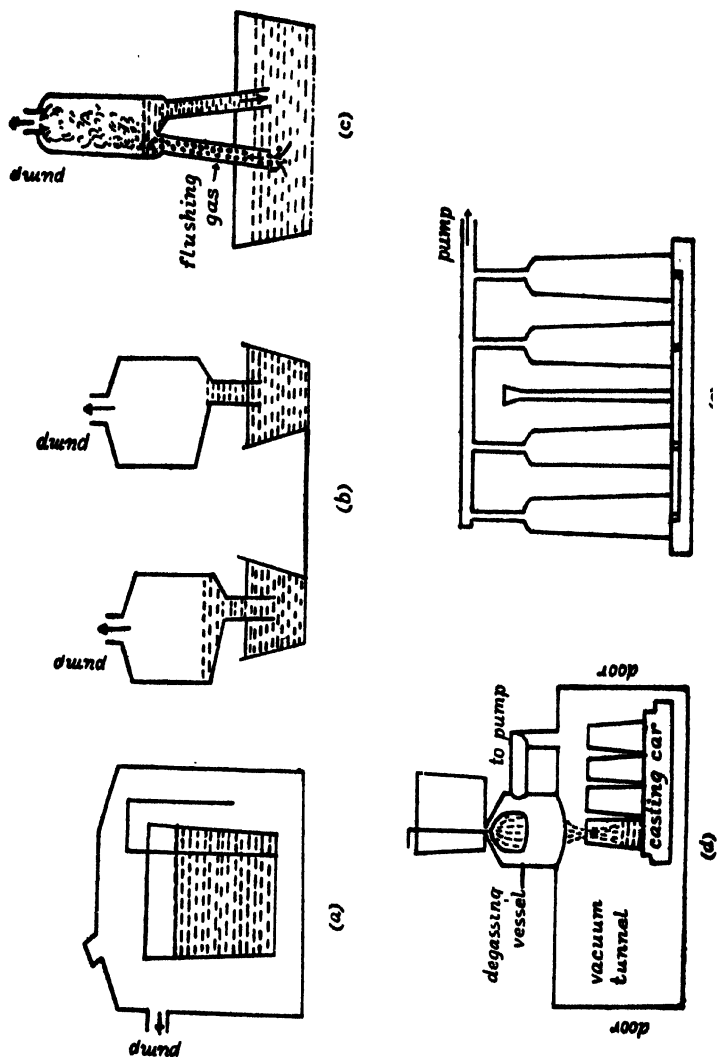


Fig. 13.3—Vacuum degassing processes—(a) ladle degassing, (b) ingot lift, (c) stream degassing and (d) vacuum lift.

There are numerous other devices which are being used but they embody the main principles discussed above. The reader may refer to the original works.¹⁵

Vacuum melting: Steel may itself be made under vacuum. This may, however, be done only in the induction or electric-arc

furnaces. Very low contents of hydrogen, nitrogen and oxide inclusions have been reported.

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